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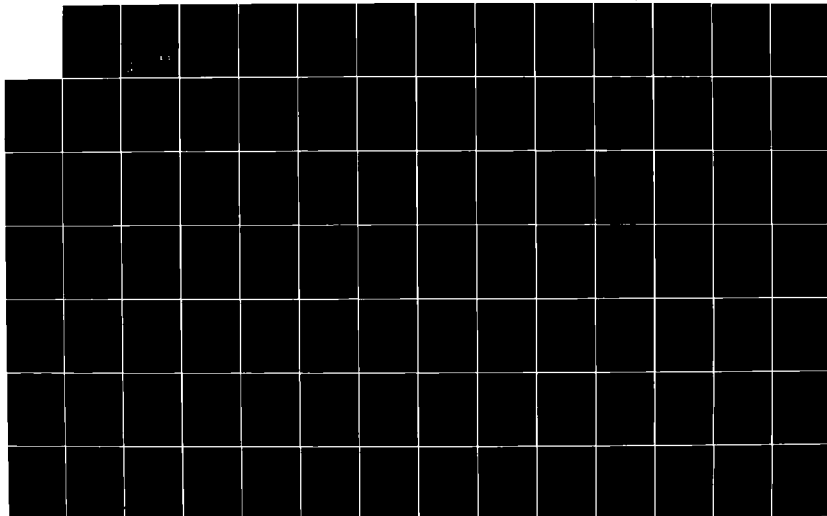
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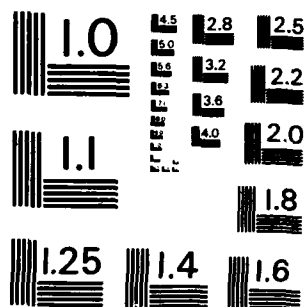
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SEMI-CONDUCTORS IN SEMICONDUCTORS

Final Technical Report

By

R.E. WILLIAMS and M.E. PATTERSON

NOVEMBER 1963

**UNITED STATES ARMY
RESEARCH AND STANDARDIZATION GROUP (EUROPE)
(EUROPEAN RESEARCH OFFICE)
LONDON ENGLAND**

CONTRACT NUMBER: DAJ37-60-C-0491

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
	AD-A136 109	
4. TITLE (and Subtitle)	5. TYPE OF REPORT & PERIOD COVERED	
Metal contacts in semiconductors	Final technical report Sep 80 - Sep 83	
	6. PERFORMING ORG. REPORT NUMBER	
7. AUTHOR(s)	8. CONTRACT OR GRANT NUMBER(s)	
Professor R.H. Williams and Dr. M.H. Patterson	DAJA37-80-C-0493	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
The New University of Ulster, Coleraine Co. Londonderry, Northern Ireland BT52 1SA	6.11.02A 1T161102BH57.07	
11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE	
USARDSG-UK 4th floor Edison House, 223 Old Marylebone Road, London NW1	November 1983	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	13. NUMBER OF PAGES	
	114	
	15. SECURITY CLASS. (of this report)	
	UNCLASSIFIED	
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report)		
Approved for public release. Distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
Semiconductor surfaces, Photoelectron spectroscopy, Auger electron spectroscopy, Schottky barriers, Ohmic contacts, Defects in semiconductors, Cadmium telluride, Indium phosphide, Gallium arsenide, Gallium Selenide.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
<p>The application of modern "surface science" experimental techniques to probe free semiconductor surfaces and their interfaces with gases and metals has enabled a much greater understanding of the role that imperfections, defects etc. play in the formation of Schottky barriers and related devices.</p> <p>In section 1 of this report we detail the interactions between various metals and vacuum cleaved and air cleaved (110) surfaces of CdTe. For metal-</p>		

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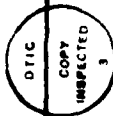
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vacuum cleaved CdTe interfaces we show that the interfaces formed are very non abrupt with interface widths in some cases exceeding twenty five angstroms. Also, provided one eliminates the systems where cadmium outdiffusion into high work function metals occurs then good agreement between the linear interface model in the Schottky limit and the data occurs. Where cadmium outdiffusion into high work function metals does occur it is postulated that Fermi level pinning in the band gap occurs due to the formation of doubly charged cadmium vacancies. The presence of an interfacial layer, due to oxidation or due to deposition of very thin ($< 2\text{\AA}$) aluminium layers, between the vacuum cleaved CdTe surface and the metal overlayer drastically effects the Schottky barrier height. Oxidation of the surface prior to metal deposition always leads to an increase in Schottky barrier height. The deposition of ultra thin aluminium layers between the CdTe surface and the metal overlayer produced effects which varied with the thickness of the aluminium interlayers. The complexity of these systems, though, are such that much more data will be needed to establish the mechanisms responsible for these effects.

In Section 2 of this report we consider the role of surface defects in the pinning of the Fermi level at free semiconductor surfaces and in the adsorption and oxidation processes involved when these surfaces interact with gases and metals. The role of imperfections at metal-semiconductor interfaces, in chemical interactions and in the determination of electrical characteristics is discussed. It is shown that there are conflicting views in the literature and some of these unresolved views are discussed.

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SECTION 1

Metal Contacts to CdTe

1:0 INTRODUCTION

In this section the results are presented for barriers fabricated on low resistivity CdTe samples. The CdTe crystals used were: In doped n-type crystals grown by the Fast Vertical Bridgman technique described in a previous report²⁶. Sample parameters were typically : mobility $\sim 500\text{cm}^2\text{V}^{-1}\text{S}^{-1}$; carrier concentration $\sim 10^{17}\text{cm}^{-3}$; resistivity $\sim 1-10\ \Omega\cdot\text{cm}$. Crystals were grown using a Cd over pressure of 2.1 atmospheres and an indium dopant concentration of $2 \times 10^{18}\text{atom}\cdot\text{cm}^{-3}$. The crystals were slow cooled after growth. It was reported previously²⁶ that attempts at fabricating Schottky barriers on CdTe resulted in large variations in the reported values of barrier heights. One reason for this may lie in the use of so many different types of surface preparation prior to metal deposition. As was shown in the previous report²⁶ many of the surface preparations commonly used frequently leave the CdTe surface either oxidised or even depleted of one of the constituent species. It is not surprising then that a variation in the barrier heights of metal contacts on these surfaces is seen. To reduce the problems associated with these surface variations the metal contacts in the work that follows have been evaporated onto the two most reproducible types of CdTe surface i.e. the ultra high vacuum cleaved (110) surface and the air cleaved surface exposed for 48 hours to air at a pressure of one atmosphere.

1:1 EXPERIMENTAL METHOD

The method of experimentation used involves carrying out complementary surface investigations sequentially on

the same sample in the same ultra high vacuum chamber without breaking the vacuum. The techniques of XPS, AES, LEED, UPS, I - V and C - V variation were used. The approach to the metal semiconductor formation investigation is twofold. Firstly controlled amounts of metal, from fractions of a monolayer upwards are evaporated onto the surface of CdTe. The early stages of Schottky barrier formation were then monitored by XPS, UPS and AES. Once a thick metal overlayer had been established the Schottky barrier heights were measured in situ by I - V and C - V techniques. LEED was used to determine the degree of order in the metal overlayer.

In all cases the results presented are for metal-CdTe interfaces fabricated at room temperature.

1:2 RESULTS

1: The Vacuum Cleaved (110) Surface of CdTe

(a) Gold (Au).

Fig. 1.1 shows the dark current voltage characteristics of a typical Au - vacuum cleaved CdTe Schottky diode. Barriers measured for several such diodes ranged from $\phi_{bn} = 0.92\text{eV}$ to 0.98eV with n , the ideality factor varying from 1.1 to ~ 1.5 . The most typical value though was $\phi_{bn} = 0.96\text{eV}$ with $n = \sim 1.1$. A rectification factor of $10^2 - 10^3$ was typically seen on the application of $\sim 0.2\text{V}$.

Capacitance-voltage measurements, made at 10KHz , were made on the devices. A typical result is shown in fig. 1.2. The $\frac{1}{C}^2$ versus V plot is very linear up to 1V indicating a uniform doping profile in the semiconductor. The slope of the plot gives a value of the doping density, N_d , which for this diode was in good agreement with the bulk doping

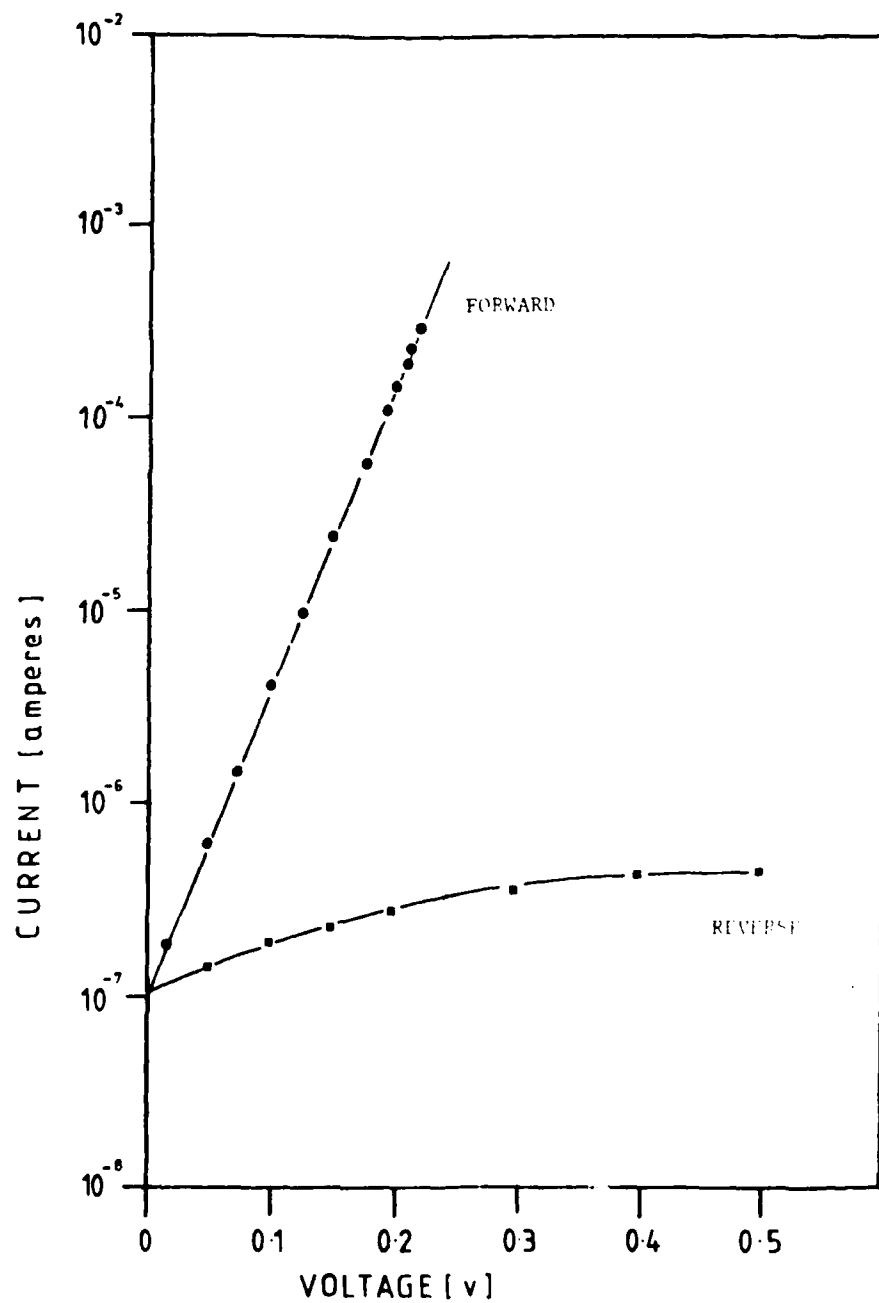


Fig. 1: Typical current - voltage characteristic (d.c.) for CdTe on the 0.01 cm^2 cleaved surface of CdTe .
 $V_0 = 0.92 \text{ V}$, $n = 1.1$.

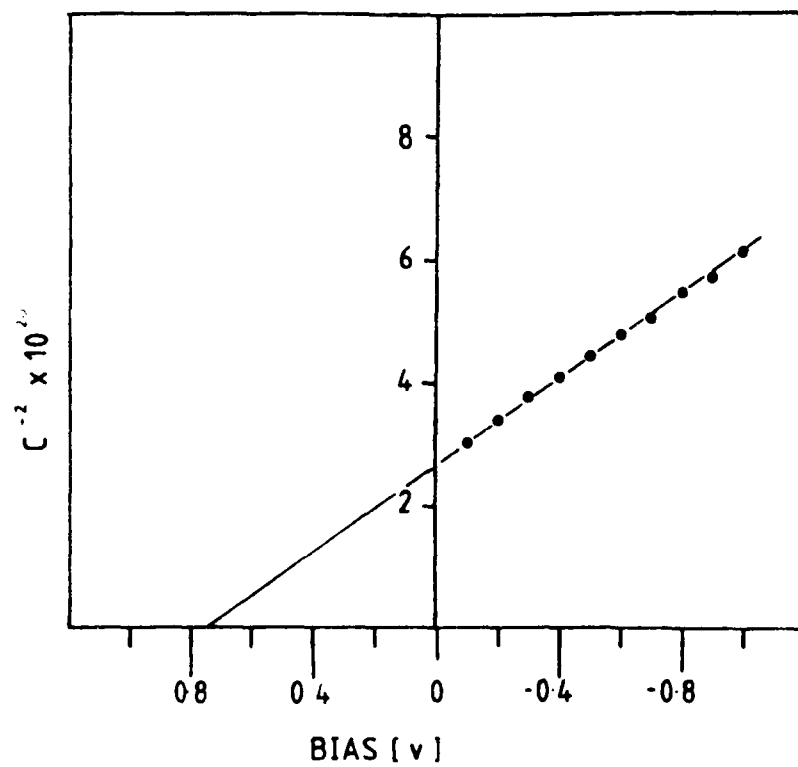


Fig. 1:2 : A typical $1/C^2$ versus applied bias plot for Au on the vacuum cleaved CdTe (110) surface. $V_i = 0.76\text{eV}$; $N_d = 6.6 \times 10^{14}\text{cm}^{-3}$; $\phi_b = 0.96\text{eV}$.

density as measured by the Hall effect. For all diodes fabricated good agreement between I - V and C - V values of barrier height was obtained.

Fig. 1.3 shows the UPS spectra obtained during the formation of a Au-CdTe diode. Spectra shown are angle resolved photoelectron spectra for normal emission. He I radiation of energy 21.2eV was used, the angle of incidence of radiation to the crystal surface being 55°. Evaporation times shown are in seconds. Spectrum 1 is the UPS spectrum of the vacuum cleaved CdTe. The various peaks may be understood, to a first approximation anyhow, in terms of bulk electron states¹. Particularly prominent is the emission from the spin orbit split cadmium 4d level at binding energies of ~10.9 and 11.5eV. Upon progressive deposition of Au these levels shift to lower binding energies by ~0.85eV, while at the same time the energy separation of the spin orbit split components remains unchanged. Emissions from these Cd 4d levels remain a prominent feature of the spectra even for quite a thick coverage of Au. At thick Au coverages it is not possible to say anything about the Te presence by UPS since the emissions from the Au 5F orbitals mask any emissions from the Te valence levels. The shift of the CdTe features in the spectrum with increasing Au coverage is due to a Fermi level movement, at the semiconductor surface, down the band gap, indicative of the formation of a Schottky barrier of ~0.85eV. This observation is based on two assumptions. Firstly that the ultra high vacuum cleaved surface of CdTe does not have any surface states which could pin the Fermi level, such that the bands near the surface are flat. Secondly that the electron

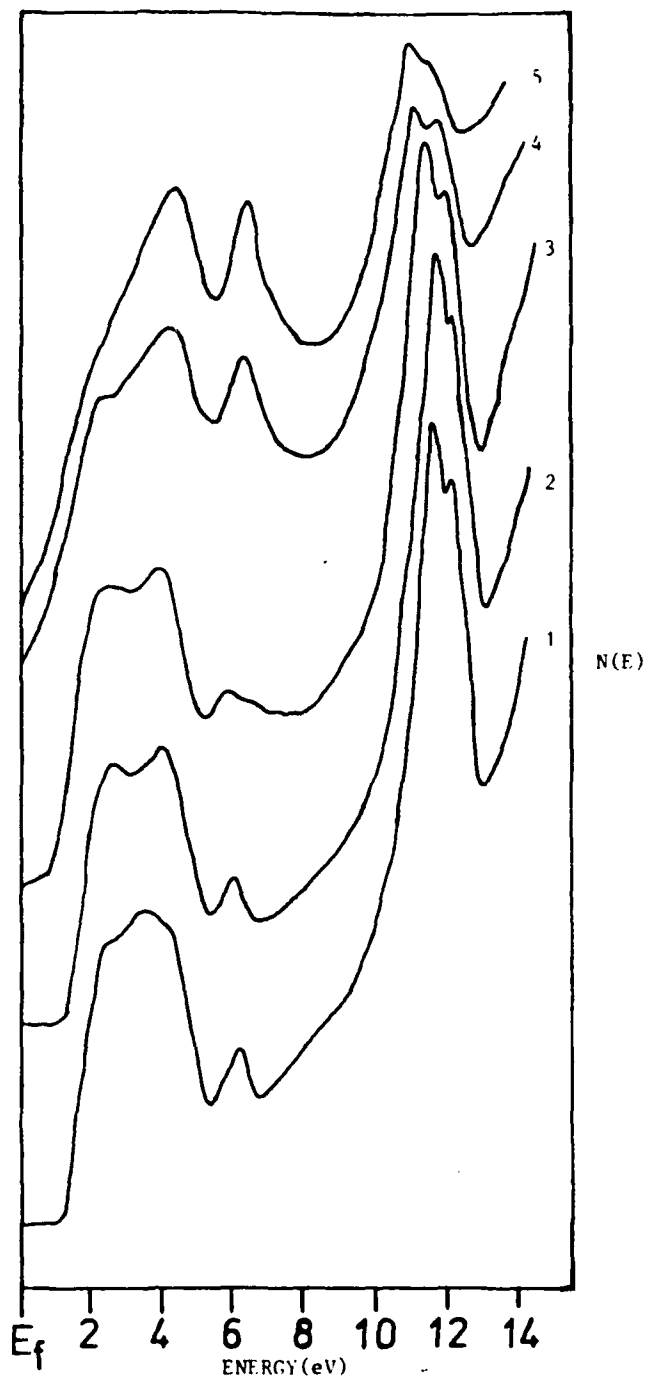


Fig. 1:3 : Angle resolved photoelectron spectra for the vacuum cleaved (110) surface of CdTe with controlled deposition of Au. Spectra shown are for normal emission, $h\nu = 21.2\text{eV}$, angle of incidence of light $\approx 55^\circ$. Spectrum 1 is of the clean CdTe surface, Spectra 2-5 are of the CdTe surface with progressive Au deposition.

escape depth i.e. the probing depth of the technique (10-20Å) is short compared to the band bending (several hundred Å) following metal deposition. The Fermi level movement at the semiconductor surface for Au deposition is summarised in fig. 1.15 along with the behaviour of other metals. This observation of band bending with increasing Au coverage is in agreement with the Schottky barrier heights established for thick film coverages by I - V and C - V techniques.

An evaluation of the contact formation by XPS and AES produced similar deposition profiles. An XPS profile is shown in fig. 1.4. This shows that initially there is a substantial fall off in the Cd and Te peak intensities, but as the Au overlayer builds up, the Cd and Te peak intensities reached some equilibrium position where relatively little decrease in peak intensity of Cd and Te was seen, even after evaporation of quite a thick Au overlayer. Slight argon ion bombardment of this interface showed that the Cd and Te atoms were incorporated within the Au overlayer rather than being situated on its outer surface.

LEED investigations of the metal overlayer showed that the overlayer was polycrystalline in nature. At no time were any ordered LEED patterns observable.

(b) Silver (Ag)

Current voltage measurements on silver-vacuum cleaved CdTe produced different behaviour from that observed for Au-CdTe systems. I - V showed that even at high bias (>1.0V) there was exhibited very little or no rectification and a linear voltage current relationship was observed indicating

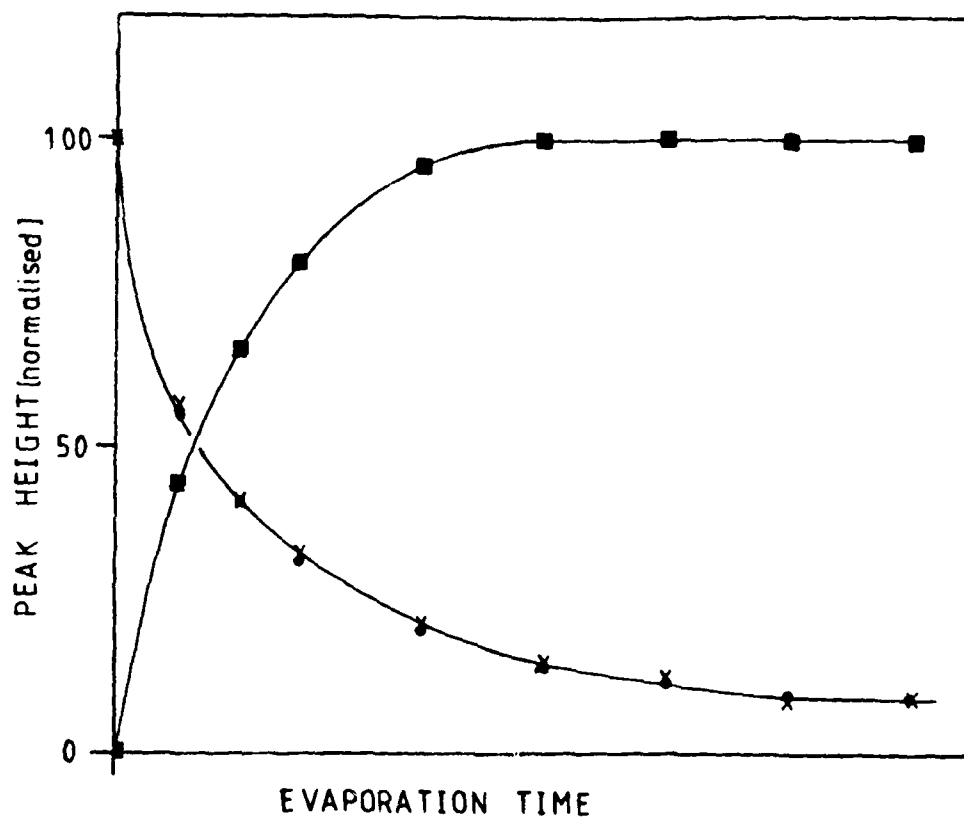


FIG. 1:4 : Deposition profile of Au deposited on the vacuum cleaved (110) surface of CdTe as measured by XPS.
 ■ = Au; ● = Te; × = Cd.

the presence of a very low ($<0.1\text{eV}$) barrier or ohmic contact. The resulting "barrier" was too low to be measured by C - V methods.

These observations were checked by evaporation of silver and gold contacts side by side onto the same vacuum cleaved CdTe surface. Where Au produced barriers as measured by I - V and C - V, of $\sim 0.96\text{eV}$ silver produced very low or ohmic contacts. UPS measurements confirmed this observation. The spectra, shown in fig. 1.5, show that as the silver is progressively deposited onto the CdTe surface no movement of the prominent Cd 4d levels occurs to a higher or lower binding energy. This concurs with the I - V and C - V results. The UPS results show another important occurrence. That is that even at high Ag overlayer thickness ($>50\text{\AA}$) emissions from the Cd 4d orbitals are still seen while those at lower binding energy, due to the Te valence levels are not apparent in the spectra. This then begs the question. How abrupt is this interface?

To probe this further AES and XPS deposition profiles were obtained during the formation of such Ag-CdTe interfaces. These are presented in fig. 1.6. XPS shows that even after deposition of more than 50\AA of Ag some Cd is still evident in the metal overlayer. While Te is lost from the probing depth of the technique at relatively thin metal overlayer coverages. Slight bombardment of the thicker Ag overlayer with argon ions showed that the excess cadmium is incorporated within the silver rather than on its outer surface.

In contrast to the XPS investigations, AES studies produced contrasting results as can be seen from fig. 1.6.

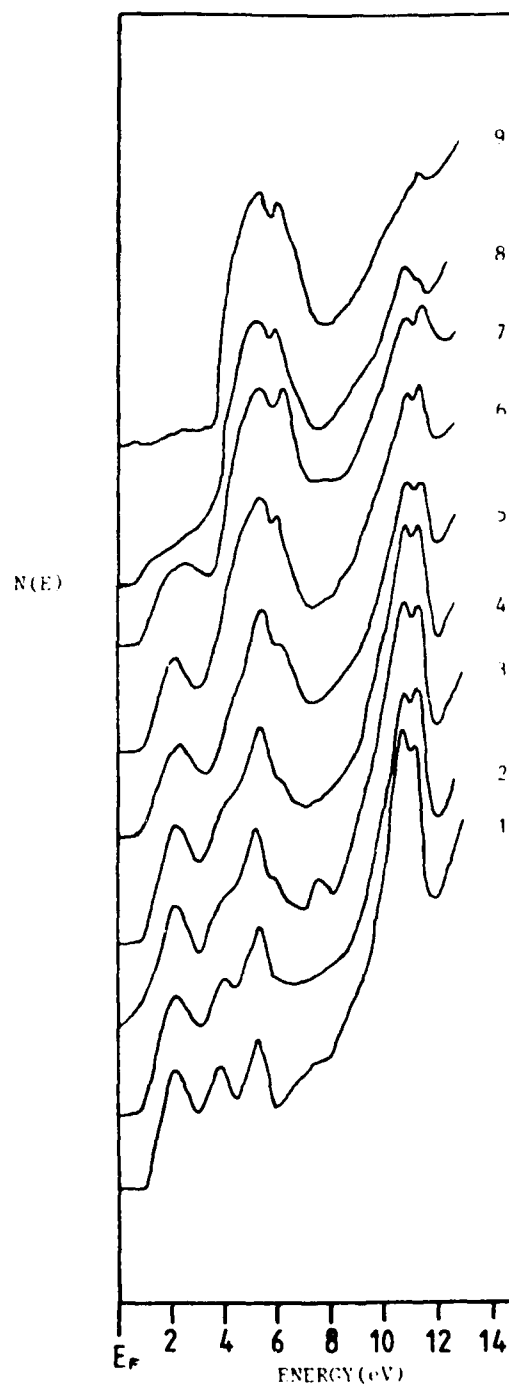


Fig. 1: Angle-resolved photoelectron spectra of the vacuum cleaved (110) surface of n-GeTe with controlled deposition of Ag. Spectra shown are for normal emission, $h\nu = 21.2$ eV; angle of incidence of light 45° . Spectrum 1 is of the vacuum cleaved surface. Spectra 2-9 are for progressive deposition of Ag.

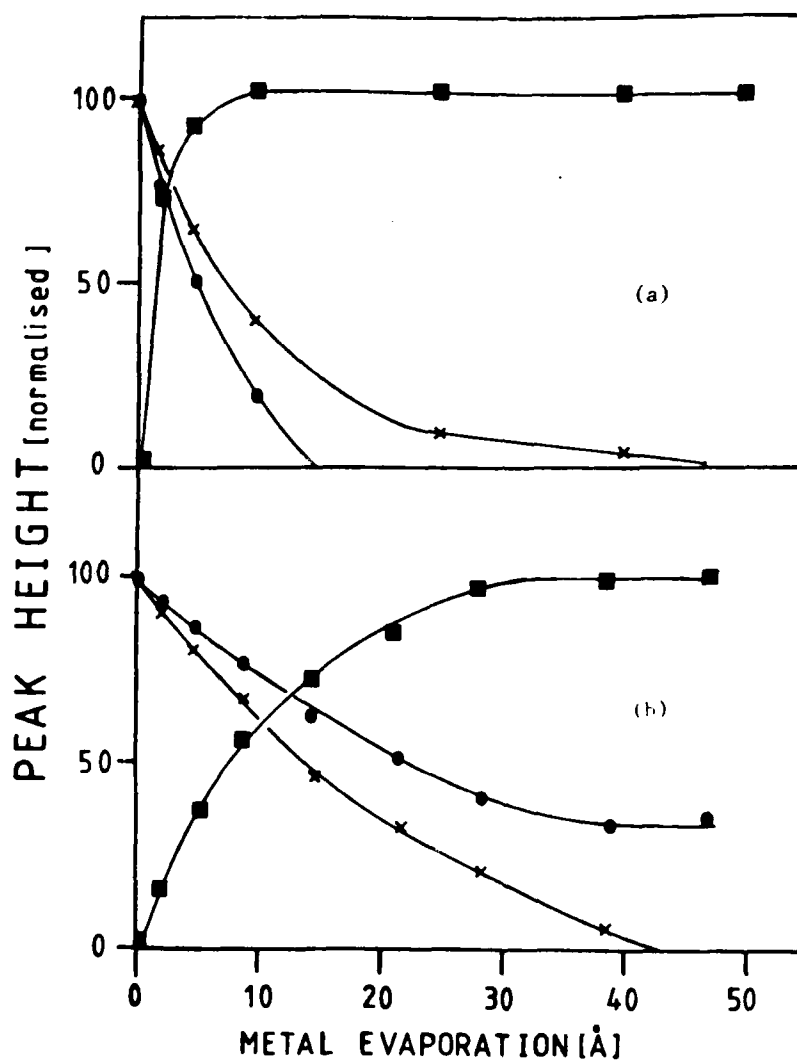


Fig. 1:6 : Deposition profiles of Ag depositing on the vacuum cleaved (110) surface of CdTe as measured by (a) XPS, (b) AES.

■ Ag; ● = Te; x = Cd

clearly the interfacial mixing process is being severely influenced by the incident electron beam used in the Auger technique. This bears out the observations of the electron beam induced disorder observed for the vacuum cleaved CdTe surface²⁶.

Clearly the emitted currents induced during XPS, of the order of 10^{-10} A, do not seem to influence the stoichiometry of the surface. These observations underline the great need for care in the application of methods and interpretation of results on materials, like CdTe, where incident electron beams are used.

LEED showed the thick silver film to be polycrystalline.

(c) Aluminium (Al)

Current voltage characteristics of Al-vacuum cleaved CdTe interfaces showed behaviour very similar to that of Ag-vacuum cleaved CdTe interfaces i.e. very low barrier (<0.1 eV) or ohmic in nature. No rectification was seen in the I - V characteristics even up to a bias of 1.5V. These observations were also checked by evaporation of Al contacts and Au contacts onto the same vacuum cleaved surface of CdTe. Au contacts produced typically barriers of ~ 0.96 eV yet all the Al contacts proved to be ohmic.

An UPS investigation of the formation of Al-vacuum cleaved CdTe interfaces produced an as yet previously unseen type of behaviour. The spectra are shown in fig. 1.7. Upon deposition of Al several things of note happen: i) at very low Al coverage, before any modification of emission in the valence band region occurs all features in the spectrum due to CdTe shift to higher binding energies by ~ 0.2 eV. ii) as the Al coverage is increased so the features

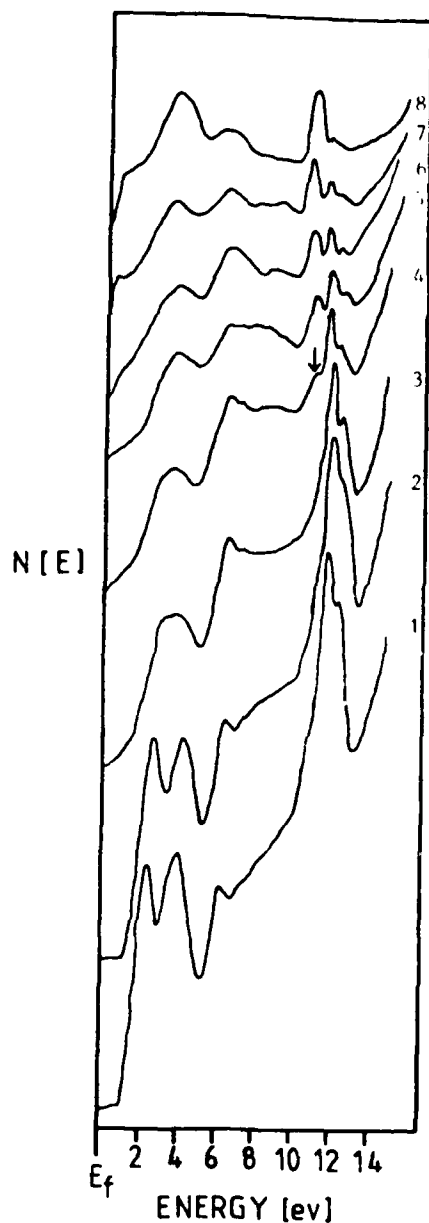


Fig 1:7 : Angle resolved spectra of the vacuum cleaved (110) surface of CdTe with progressive deposition of Al. Spectrum 1 is of the clean surface of CdTe, spectra 2-8 are with the progressive deposition of Al. Spectra measured are for normal emission, angle of incidence of light = 55°. $h\nu=21.2\text{eV}$. The new peak, indicated by an arrow, appearing in spectrum 4 and subsequent spectra is due to "free" Cd.

move back to their original binding energies. iii) at higher Al coverage one sees a new component appearing on the lower energy side of the Cd 4d emissions by $\sim 0.6\text{eV}$. As the Al coverage increases this feature becomes very dominant. This new 'Cd' peak is due to chemically shifted emission from the Cd 4d orbitals of Cd which has been removed from the semiconductor surface and incorporated in the metal overlayer. The Fermi level movement associated with the interface formation is summarised in fig. 1.15. It is known that Al can act as a shallow donor in bulk CdTe^2 . If one assumes that if on an initial indiffusion of Al atoms into the surface layers of the CdTe similar shallow donor levels accrue then the initial behaviour seen with UPS is consistent with the indiffusion of Al to form a highly n-type surface layer with the Fermi level being located near to the conduction band edge. As the metal contact grows on the surface then charge transfer now occurs from these shallow donors resulting in the Fermi level moving back down the band gap. XPS deposition profiles indicate a similar type of behaviour as is seen with UPS. Initially both Cd and Te reduce at about the same rate. However at larger Al coverages the emissions due to Cd increase compared to the Te emissions, consistent with the out diffusion of the Cd atoms (see fig. 1.8).

LEED investigations of the thick Al film at no time showed a recognisable pattern indicating that the metal overlayer was polycrystalline.

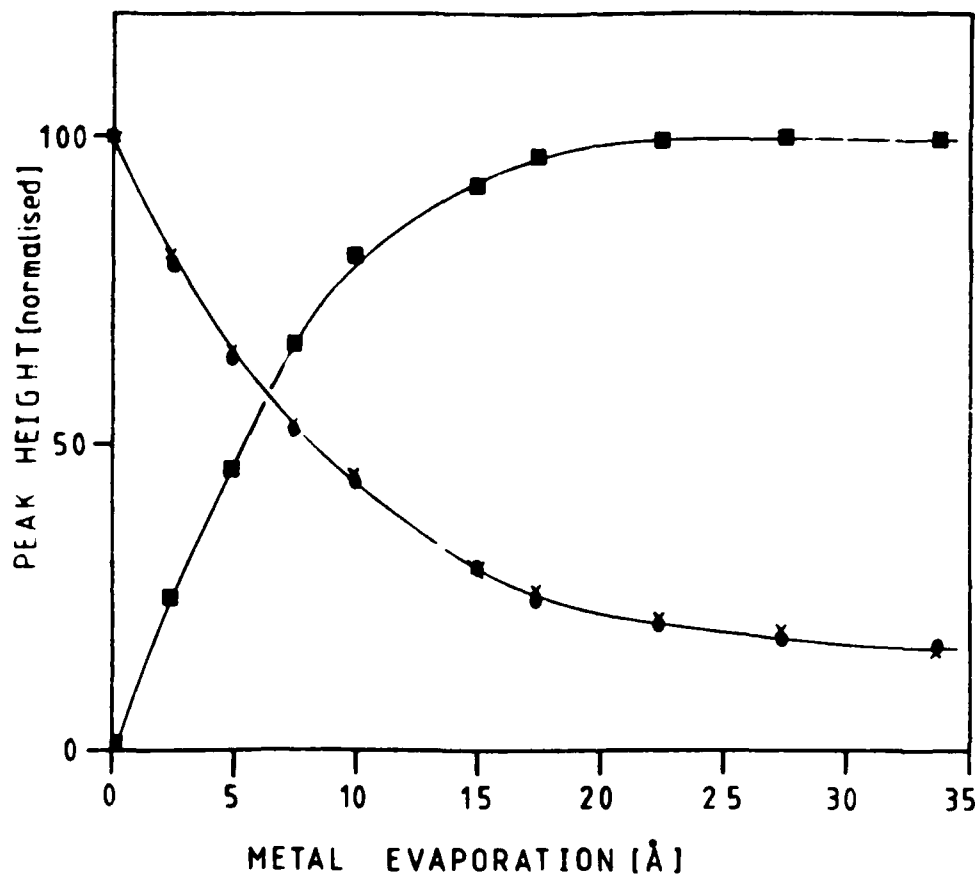


Fig. 1:8 : Deposition profile for Al depositing on the vacuum cleaved (110) surface of CdTe as measured by XPS.

■ = Al ; ● = Te ; x = Cd.

(d) COPPER (Cu)

I - V and C - V measurements of Cu-vacuum cleaved CdTe Schottky barriers yielded barrier heights of 0.43eV to 0.46eV. I - V produced barriers generally of the order 0.43eV to 0.44eV with n values of ~1.05 to 1.1. Rectification at 0.5V was ~100-200. C - V measurements produced barriers typically slightly higher than the I - V measurements at 0.44eV to 0.46eV. The slope of the C^{-2}/V plots were fairly linear indicative of a uniform doping profile in the semiconductor.

UPS measurements taken for deposition of Cu on vacuum cleaved CdTe are presented in fig. 1.9. Two main occurrences are important here. Firstly all the peaks in the spectra appear to shift to lower binding energies by ~0.2eV as the copper overlayer is gradually built-up. Assuming, as in the case of Au, that the bands near the atomically clean surface are flat, then this may be interpreted as a movement of the Fermi level at the surface of the CdTe down the gap away from the conduction band by ~0.2eV, consistent with the formation of a Schottky barrier, as measured by I - V and C - V of ~0.45eV. Secondly the appearance at a binding energy of ~10.3eV i.e. ~0.6eV down from the Cd 4d position in CdTe, at high metal overlayer thickness of a small peak due to Cd atoms from the CdTe substrate being incorporated within the Cu overlayer. The emissions from the Cu mask the positions of the Te valence levels, and as no core levels of Te are accessible by UPS it is necessary to use XPS to ascertain the fate of Te in this interface system. The XPS deposition profile shown in fig. 1.10 shows that for deposition of a Cu overlayer greater than the probing depth

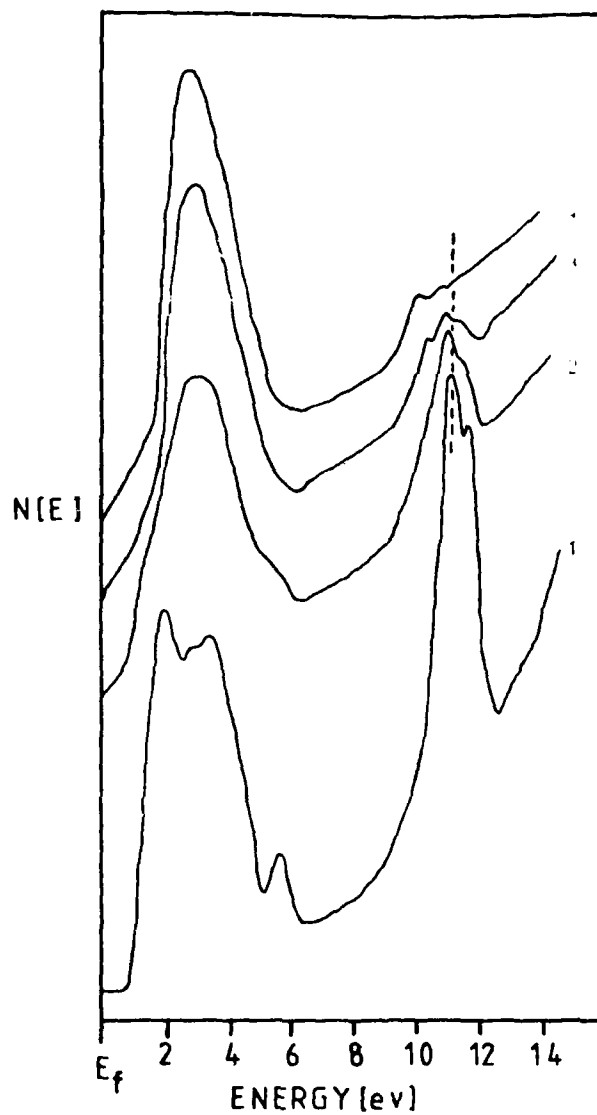


Fig. 1:9 : Angle resolved photoelectron spectra for vacuum cleaved (110) surface of CdTe with controlled evaporation of copper. Spectrum 1 is the clean surface of CdTe. Spectra 2-4 are for progressive depositions of copper. Spectra measured are for normal emission. Angle of incidence of light = 55° ; $h\nu = 21.2\text{eV}$.

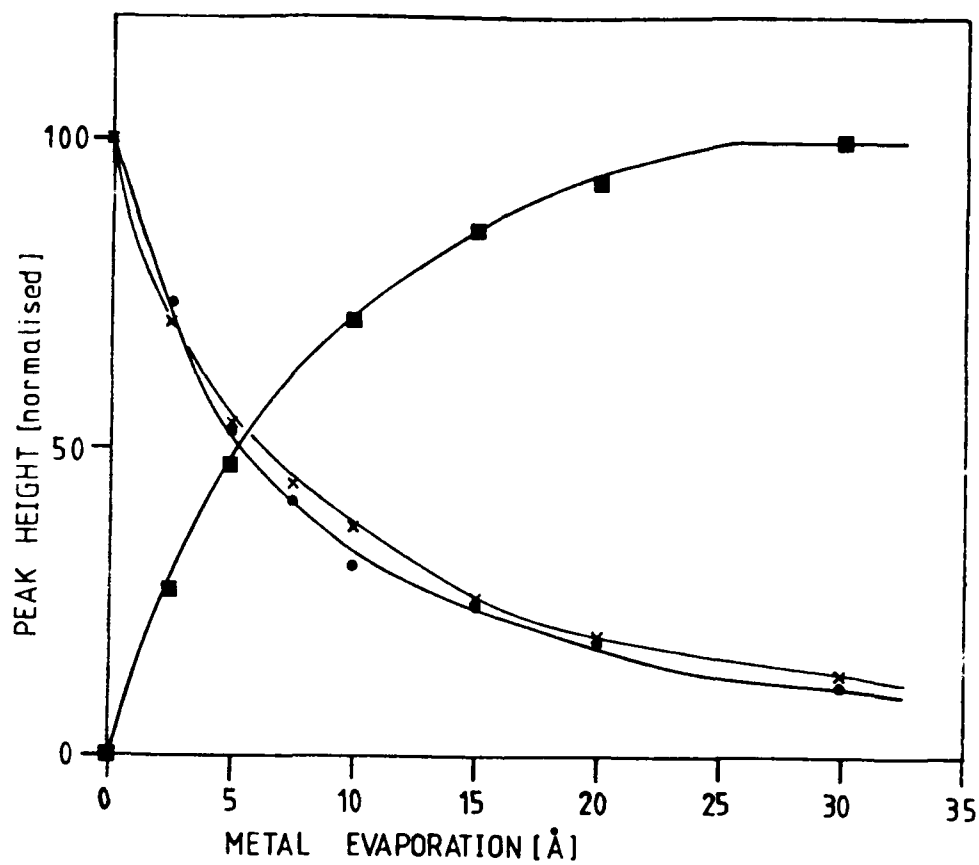


Fig. 1:10 : Deposition profile for the deposition of Cu on to the vacuum cleaved (110) surface of CdTe as measured by XPS.

■ = Cu; ● = Te; X = Cd.

of the spectrometer ($\sim 20\text{\AA}$) one still observes the presence of both Cd and Te in the metal overlayer indicating that this interface is very far from being atomically abrupt and indeed the interface region extends over many tens of angstroms.

LEED indicates that the Cu overlayer is polycrystalline.

(e) Indium (In)

Current-voltage measurements on indium-vacuum cleaved CdTe contacts showed very low barrier ($<0.1\text{eV}$) or ohmic contact behaviour. An observation that concurred well with the band bending conclusions from the UPS spectra. These spectra are shown in fig. 1.11. It should be noted that the actual binding energies of the levels in the spectrum changed, in a manner similar to that observed for Al, as the In overlayer was built-up. On deposition of small fractions of a monolayer of In the whole photoemission spectrum of CdTe moves to a higher binding energy by $\sim 0.2\text{eV}$ consistent with a shift of the Fermi level at the surface towards the conduction band by $\sim 0.2\text{eV}$. As the In overlayer builds up into a continuous film the features in the spectrum experience a move back to their original binding energies. The behaviour of In in bulk CdTe is well documented². In is known to behave as a shallow donor in bulk CdTe producing levels at $E_c - 0.014\text{eV}$. The UPS observations then are consistent with an initial indiffusion of In atoms which form these shallow donor levels at the CdTe surface resulting in a movement of the Fermi level at the surface near to the conduction band. Once the In metal overlayer builds up, charge transfer occurs from these levels to the metal and

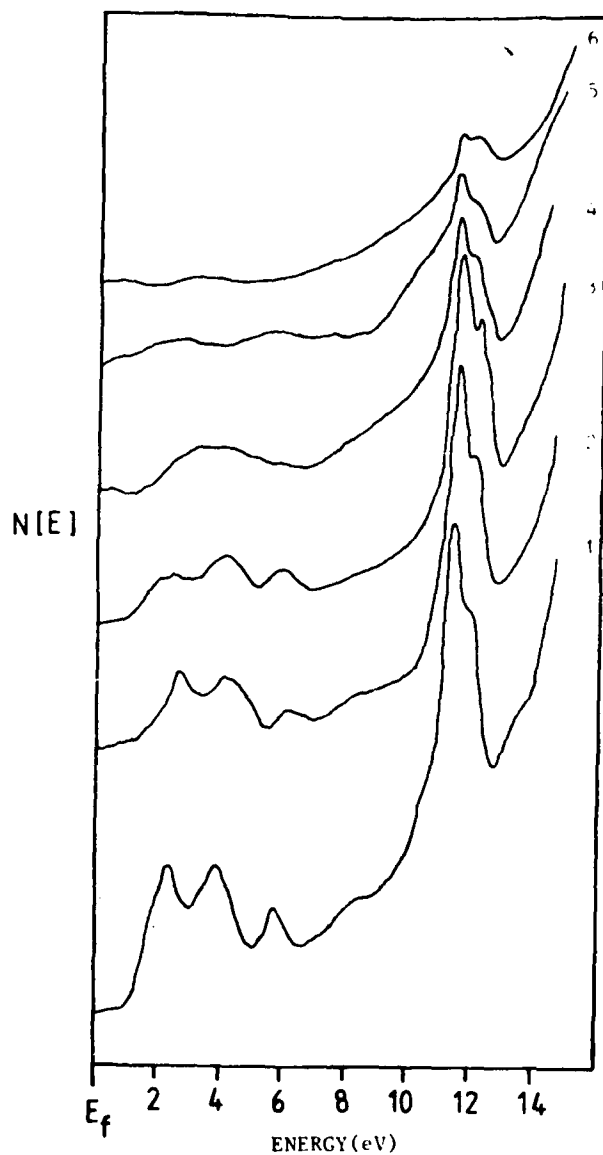


Fig. 1:11 : Angle resolved photoelectron spectra of the vacuum cleaved (110) surface of n-CdTe with controlled deposition of In. Spectra shown are for normal emission; $h\nu=21.2\text{eV}$; angle of incidence of light = 55° . Spectrum 1 is of the vacuum cleaved CdTe surface. Spectra 2-6 are of the CdTe surface with progressive deposition of In.

the Fermi level moves back to its original position. The UPS spectra show no sign of any Cd in any other form than that of CdTe.

XPS investigations of this system show that both Cd and Te reduce in intensity at the same rate as the metal overlayer builds up. However both species are still evident in the spectra after an In thickness greater than the XPS probing depth has been deposited. LEED patterns from the metal overlayer were not observed and it may thus be concluded that the metal overlayer is polycrystalline.

Hence UPS and XPS would both indicate that the In-CdTe interfaces are also far from being abrupt with indiffusion of In being prevalent.

(f) TIN (Sn)

Current voltage and capacitance voltage measurements of tin-vacuum cleaved CdTe Schottky barriers yielded barrier heights in the 0.4 to 0.44eV range. I - V measurements on several diodes produced barrier heights varying from 0.40eV to 0.43eV with n values of 1.1 to 1.3. Rectification, at a bias of 0.5V, was typically of the order of 10^2 to 3×10^2 . C - V values for ϕ_b were usually slightly higher than I - V measurements with typical values being 0.42eV to 0.44eV.

UPS measurements during the formation of a tin-vacuum cleaved CdTe interface produced a unique behaviour pattern. This is reflected in fig. 1.15 where the Fermi level behaviour is monitored as a function of metal coverage. The actual UPS spectra are shown in fig. 1.12. Two main things happen as the tin is deposited onto the CdTe surface. Firstly, following the deposition of small fractions of a

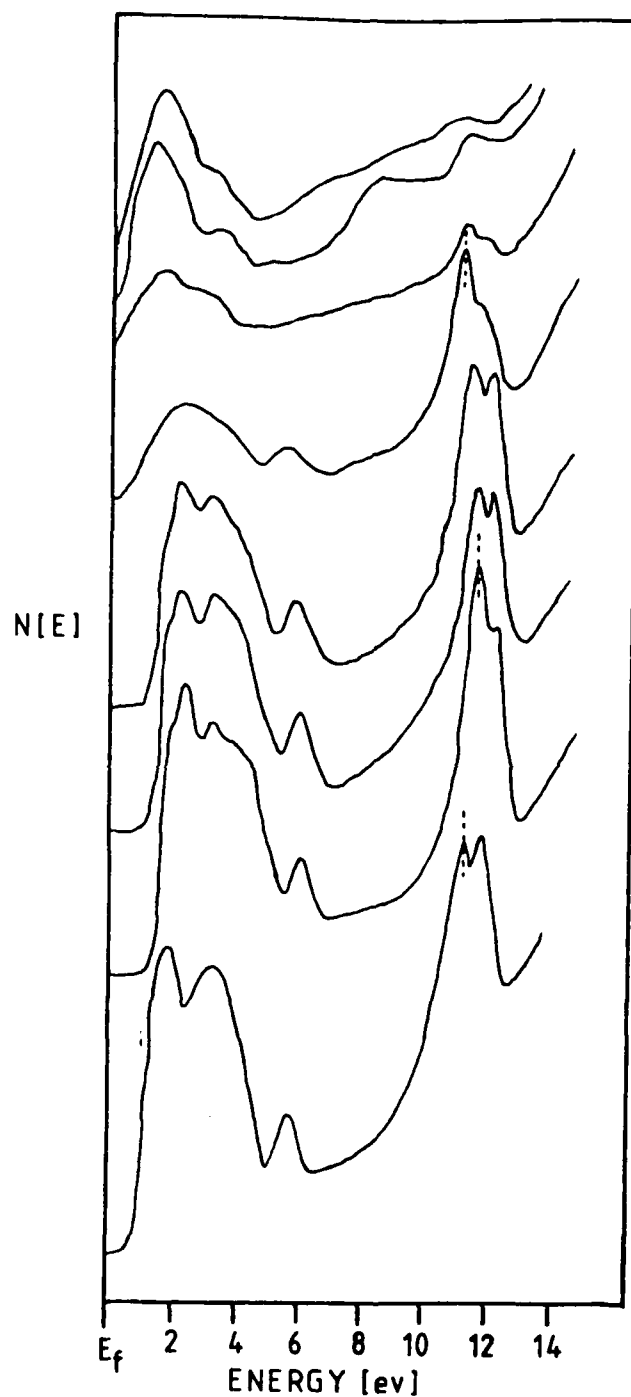


Fig. 1:12 : Angle resolved photoelectron spectra for the deposition of Sn onto the vacuum cleaved (110) surface of CdTe. Spectra 1 is for the clean (110) surface, spectra 2-8 are for the subsequent Sn depositions. Spectra shown are for normal emission, angle of incidence of light = 55°, $h\nu=21.2\text{eV}$. The dotted line shows the position of the CdTe emissions with respect to the Fermi level at various stages of the interdiffusion.

monolayer of Sn onto the CdTe surface all features in the spectrum experience a shift to higher binding energy by $\sim 0.2\text{eV}$, consistent with a shift of the Fermi level at the semiconductor surface towards the conduction band by $\sim 0.2\text{eV}$. However as the tin overlayer develops into a continuous film on the surface the features in the spectrum experience a move to lower binding energy. The movement of the features stops at a position $\sim 0.3\text{eV}$ lower in binding energy than the binding energies of the clean CdTe, with the assumed flat band condition. This indicates that for a thick Sn overlayer band bending of $\sim 0.3\text{eV}$ has occurred, a result which is in agreement with the I - V and C - V measurements of Schottky barrier height. The behaviour of Sn as a dopant in CdTe is very uncertain. Unlike In and Al, which are known to produce shallow donors in bulk CdTe at $E_c - 0.014\text{eV}$,² the energy levels associated with Sn are not well documented. Sn is known to behave amphotERICALLY in CdTe depending on whether it substitutes for a Te or Cd atom³. If one assumes that it behaves as a shallow donor then the observation of the Fermi level movement towards the conduction band on deposition of fractions of a monolayer of Sn can be attributed to the formation of shallow donors due to indiffusion of the Sn atoms. As the Sn overlayer builds up on the surface charge transfer to the Sn from these shallow donors occurs, resulting in the Fermi level moving back down the gap by $\sim 0.5\text{eV}$ consistent with the Schottky model of Schottky barrier formation. No free Cd or Te was seen by UPS. An observation which was corroborated by XPS, which showed the reduction in Te and Cd presence within the probing depth of the XPS at an equal and consistent rate. LEED showed the Sn overlayer to be polycrystalline.

(g) Nickel (Ni)

I - V and C - V measurements on nickel-vacuum cleaved CdTe surfaces yielded Schottky barrier heights of $\sim 0.4\text{eV}$. I - V gave a range of values of 0.38eV to $\sim 0.41\text{eV}$ with n values of ~ 1.1 to 1.3 . Rectification values of ~ 80 - 120 were recorded for a bias of 0.5V . C - V measurements produced barriers of $\sim 0.4\text{eV}$ with fairly linear plots indicating a fairly uniform doping profile within the CdTe surface. Figure 1.13 illustrates the deposition of Ni on (110) CdTe as observed by UPS. Spectrum 1 is of the vacuum cleaved surface of CdTe. Subsequent spectra show that as the Ni is deposited several things happen. Firstly all features corresponding to emission from CdTe shift to lower binding energies by $\sim 0.4\text{eV}$ as the Schottky barrier forms, an observation consistent with I - V and C - V. Secondly the emission in the valence band region is modified as emission from the Ni become dominant. Thirdly the emission corresponding to the Cd 4d levels is split with a new component appearing at a binding energy smaller than the binding energy of Cd in CdTe, by $\sim 0.6\text{eV}$. This is from Cd atoms removed from the CdTe and being incorporated in the Ni overlayer. This observation is given credence by the deposition profile as measured by XPS, figure 1.14. This shows a considerable Cd presence in the metal overlayer even after deposition of a thick ($>50\text{\AA}$) film of Ni.

The barrier behaviour of the various metal-vacuum cleaved CdTe interfaces studied here are summarised in table 1.1.

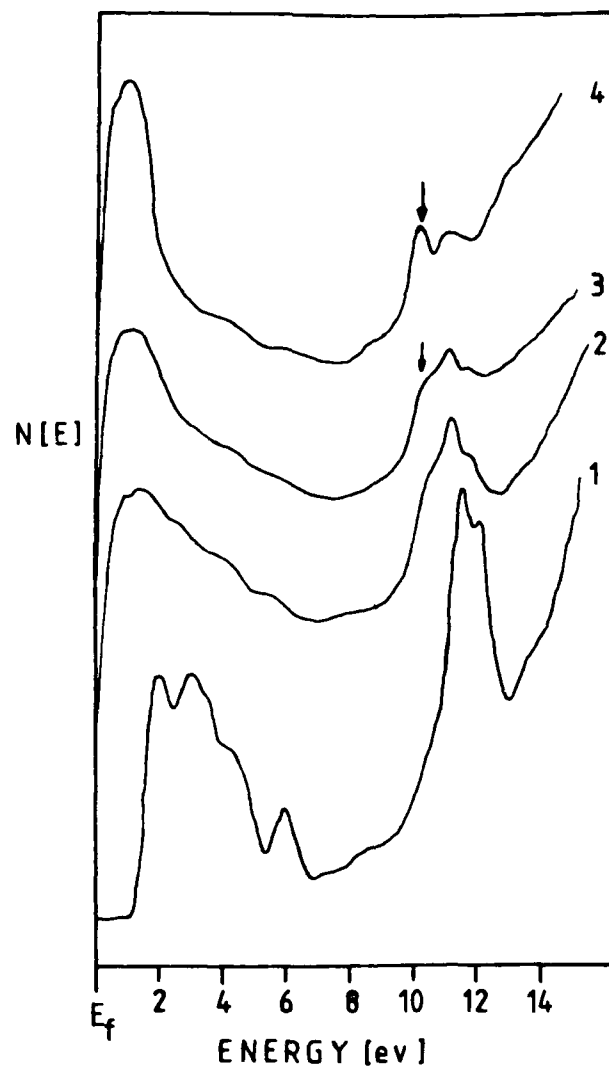


Fig. 1:13 : Angle resolved photoelectron spectra of the vacuum cleaved (110) surface of n-CdTe with controlled emission of Ni. Spectra shown are for normal emission; $h\nu=21.2\text{eV}$; angle of incidence of light $=55^\circ$. Spectrum 1 is of the vacuum cleaved CdTe surface. Spectra 2-4 are for the vacuum cleaved surface with progressive Ni depositions. The peak appearing in spectra 2-4, marked with an arrow, is due to "free" Cd.

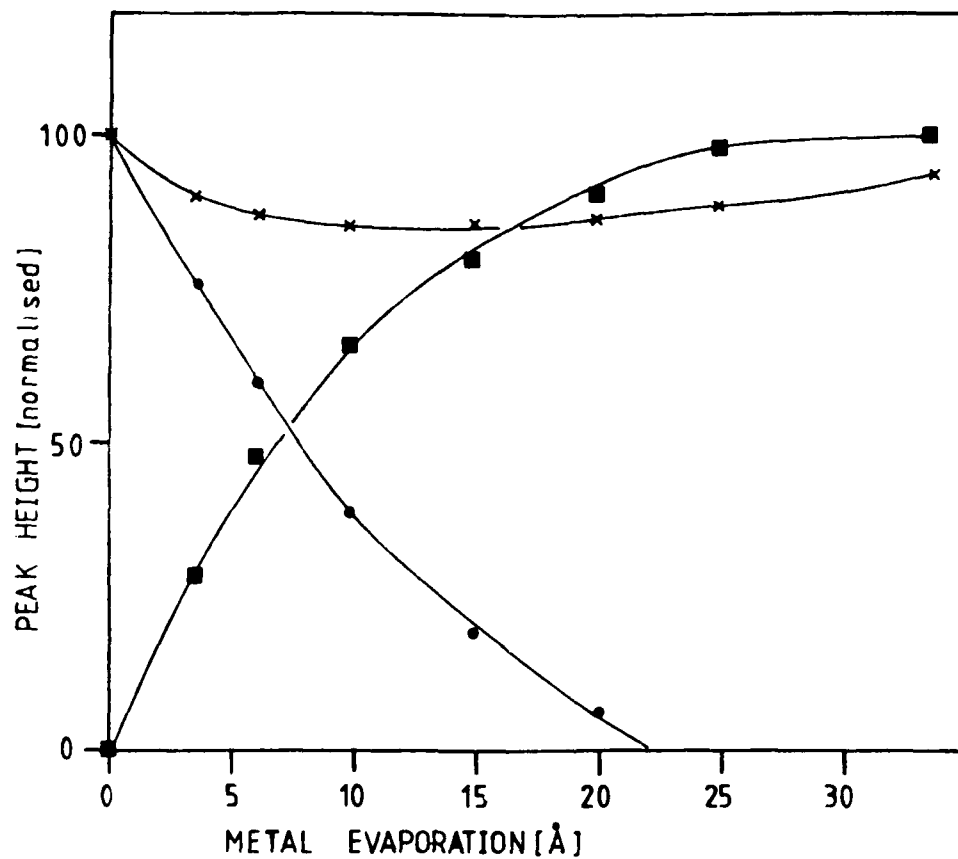


Fig. 1:14 : Deposition profile of Ni depositing on the vacuum cleaved (110) surface of CdTe as measured by XPS.

■ = Ni; X = Cd; ● = Te.

Metal	$\phi_{B.v.c.}(eV)$			Typical $\phi_{B.v.c.}$ (eV)	$\phi_m^{(25)}$ (eV)	$\phi_m^{-X_{CdTe}}$ (eV)	Cd Outdiffusion
	1-V	C-V	UPS				
Au	0.92-0.98	0.96	0.85	0.96	5.1	0.82	No
Ag	ohmic	very low	ohmic	ohmic	4.26	0	No
Al	ohmic	very low	ohmic	ohmic	4.28	<0	Yes
In	ohmic	very low	ohmic	ohmic	4.12	<0	No
Sn	0.40-0.43	0.42-0.44	0.3	0.40	4.42	0.14	No
Cu	0.43-0.44	0.44-0.46	0.2	0.45	4.65	0.37	Yes
Ni	0.38-0.41	0.40	0.40	0.40	5.15	0.87	Yes

Table 1.1: Barrier behaviour measured for the metal-vacuum cleaved interfaces investigated. The barrier height on the vacuum cleaved surface is denoted by $\phi_{B.v.c.}$. Also presented are the barrier heights predicted by the Schottky theory i.e. ($\phi_m^{-X_{CdTe}}$).

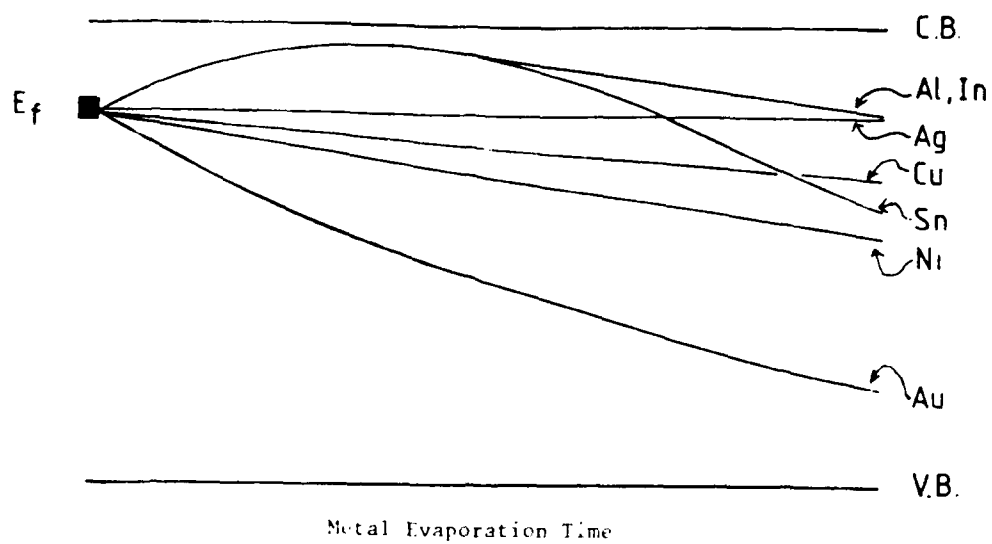


Fig. 1:11 : Fermi level movement at the CdTe surface, as measured by UPS, as various metals are progressively deposited onto the vacuum cleaved (110) surface of CdTe.

2:(ii)THE AIR CLEAVED (110) SURFACE OF CdTe

(a) GOLD (Au)

I - V and C - V measurements on gold contacts made to air cleaved CdTe showed the presence of Schottky barriers of height $\sim 1.1\text{eV}$: I - V measurements typically ranged from 0.98eV to 1.1eV with n values typically 1.0 to 1.5 . Rectification at 0.3V bias was typically 10^3 to 2×10^3 . A typical I - V profile is shown in fig. 1.16. C - V measurements produced very linear C^{-2} against V plots, see fig. 1.17, with barrier heights ranging from 1.0 to 1.15eV . UPS was not used to monitor the deposition mechanism as the information available from the UPS spectrum of the air cleaved (110) face of CdTe is not sufficient to enable peak heights and positions to be accurately monitored.

Deposition mechanisms were monitored however using XPS. A deposition profile for Au on air cleaved CdTe is shown in fig. 1.18. This shows that as the Au film builds up on the surface both Cd and Te emissions diminish. However soon Cd is lost from the spectrum and Te remains in the surface layer even after the evaporation of a thick Au film. Argon ion bombardment of this thick Au overlayer showed that the Te was incorporated in the Au overlayer.

No identifiable LEED pattern was identified for the thick Au film indicating that the overlayer is polycrystalline in nature.

(b) SILVER (Ag)

I - V and C - V measurements on the silver-air cleaved CdTe system showed marked differences in behaviour to Ag

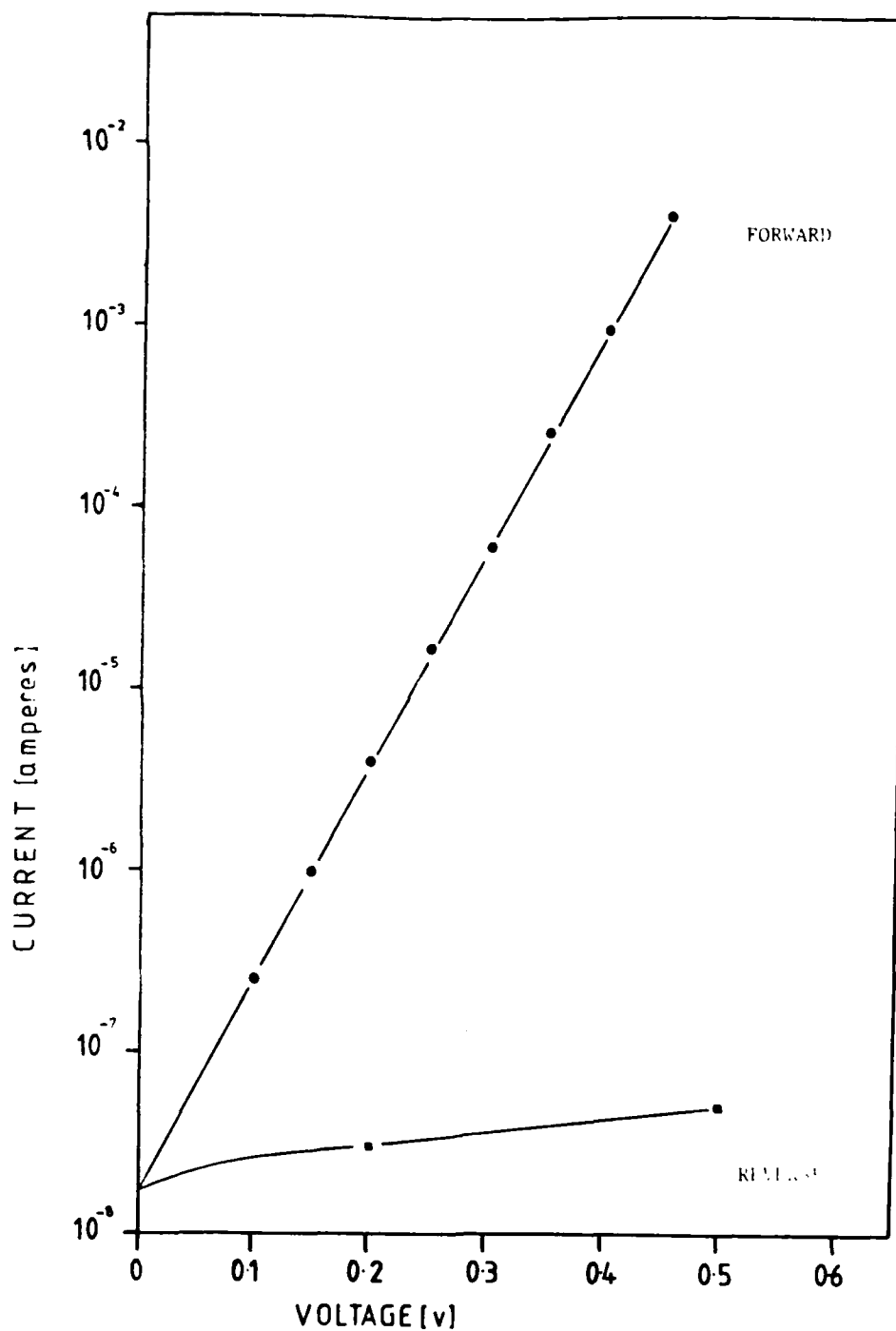


Fig. 1:16 : A typical current-voltage characteristic (d.c.) for a Au contact to the air-cleaved (110) surface of p-GdAs.

$V_{bi} = 0.45$ V, $n = 1.5$.

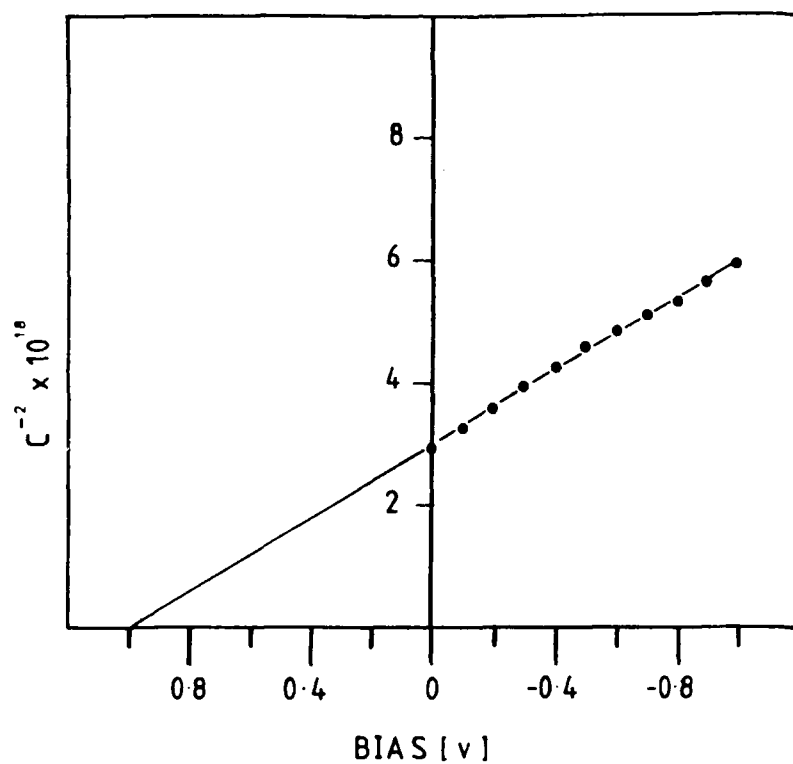


Fig. 1:17 : A typical C^{-2} versus applied bias (v) plot for a gold contact to an air cleaved (110) surface of n-CdTe.

$V_i = 1.0\text{eV}$; $N_d = 7.9 \times 10^{16}\text{cm}^{-3}$; $\phi_b = 1.1\text{eV}$.

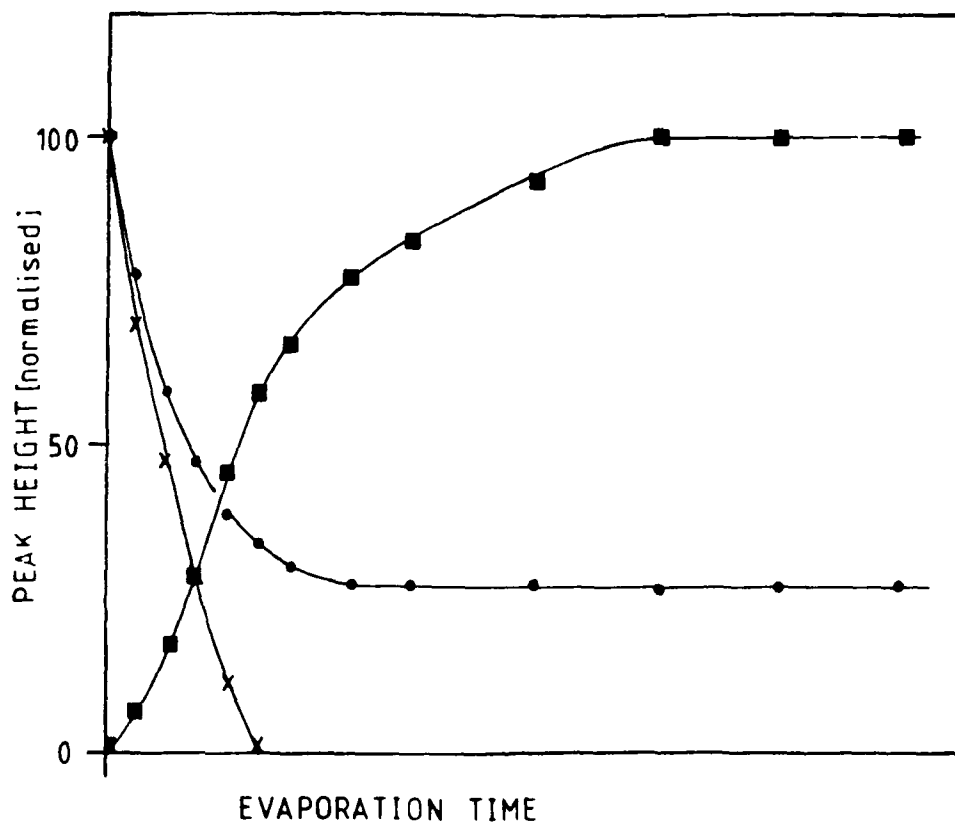


Fig. 1:18 : Deposition profile of Au depositing onto the air cleaved (110) surface of n-CdTe as measured by XPS.

■ = Au; ● = Te; × = Cd.

contacts on the atomically clean vacuum cleaved surface. Whereas on the vacuum cleaved surface ohmic contacts were produced, the effect of the oxide layer, produced by exposure of the CdTe to air prior to metal deposition, is to produce Schottky barriers of $\sim 0.53\text{eV}$. I - V measurements produced barrier heights ranging from 0.5eV to 0.57eV , with n values typically 1.0 to 1.15. Rectification at a bias of 0.5V was typically 5×10^2 to 10^3 . C - V measurements produced barriers within the range 0.53eV to 0.55eV with very linear C^{-2} versus V plots.

An XPS deposition profile is shown in fig. 1.19. This shows a similar set of events to that seen with the formation of Au - air cleaved CdTe interface. Initially as the Ag overlayer builds up so the emissions from Cd and Te diminish at approximately the same rate. However it is evident that Cd emissions disappear from the spectra while those due to Te do not. Even at thick Ag overlayer coverage there is still evidence of Te being incorporated within the Ag overlayer. An observation confirmed by argon ion bombardment of the surface. LEED showed the metallic overlayer to be polycrystalline.

(c) ALUMINIUM (Al)

Typical I - V and C - V measurements of an Al-air cleaved CdTe Schottky barrier are shown in figs. 1.20 and 1.21. I - V measurements showed barriers present of height 0.90eV to 0.93eV with n values of 1.4 to 1.5. Rectification, at a bias of 0.3V was typically of the order of 200 to 500. C - V measurements produced very linear C^{-2} versus V plots with ϕ_b ranging from 0.92eV to 1.0eV . The majority of

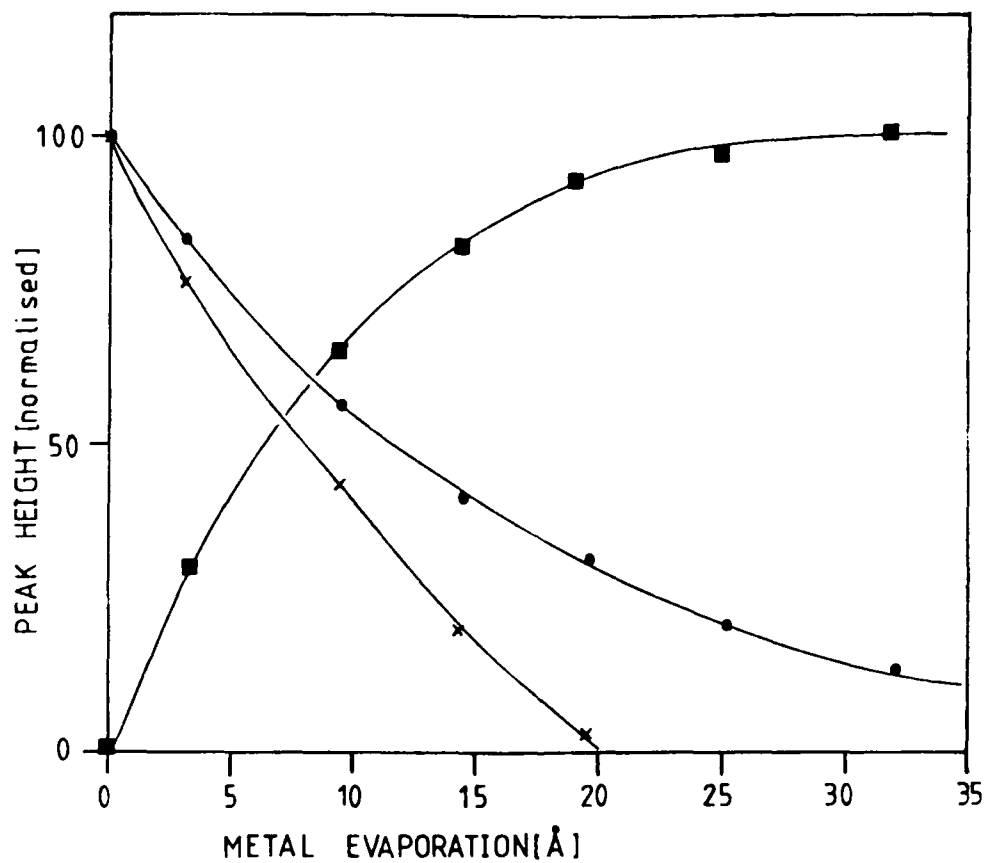


Fig. 1:19 : Deposition profile for Ag depositing on the air cleaved (110) surface of n-CdTe as measured by XPS.

■ = Ag; ● = Te; X = Cd.

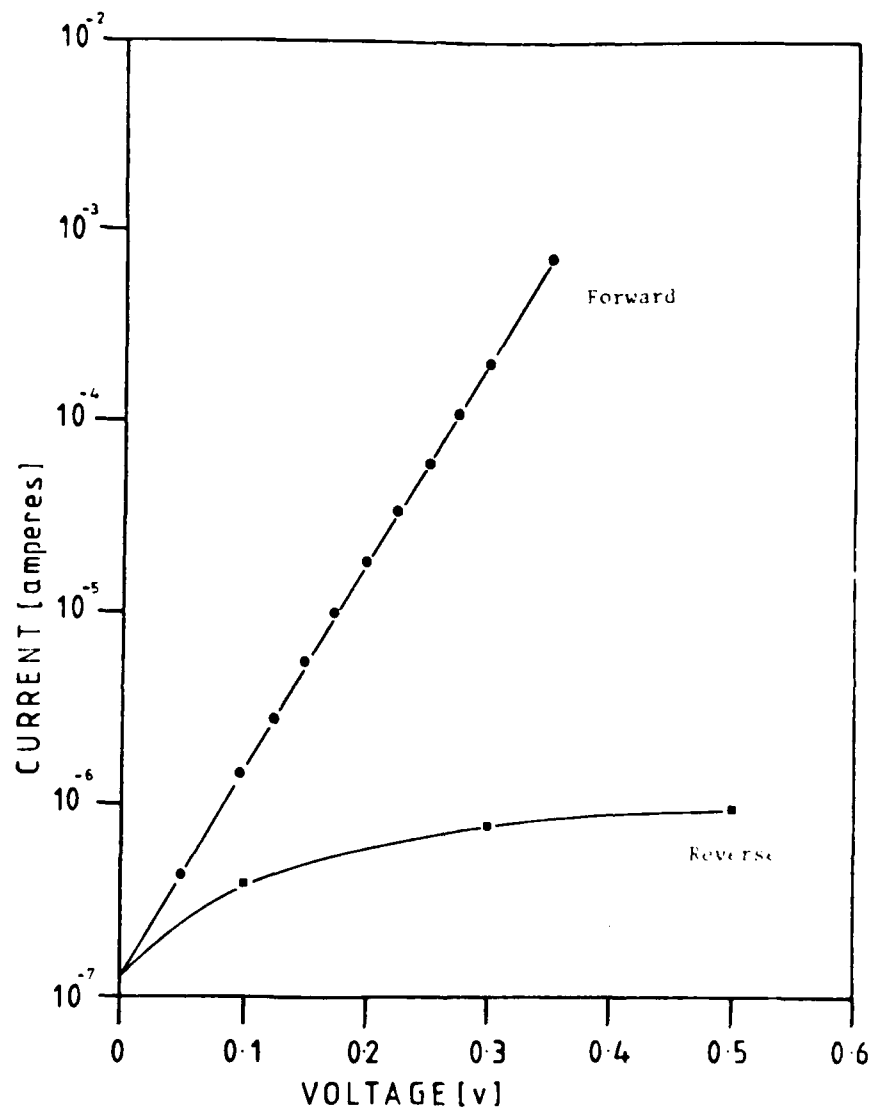


Fig. 1:20 : A typical current-voltage characteristic (d.c.) for an Al contact to the air cleaved (110) surface of n-CdTe.

$$\phi_b = 0.93\text{eV}; \quad n = 1.5.$$

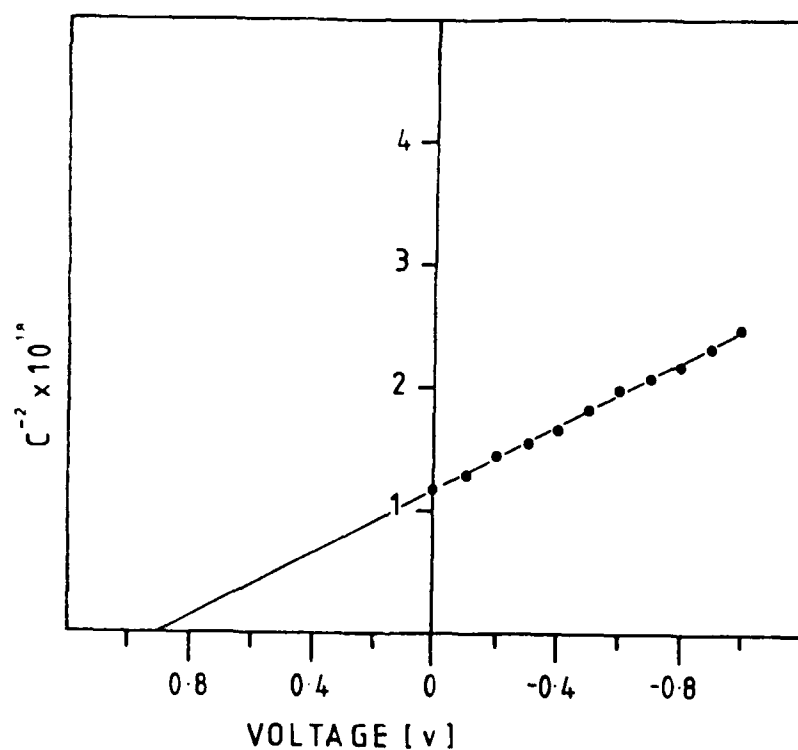


Fig. 1:21 : A typical C^{-2} versus applied bias (v) plot for an
 A. contact to an air cleaved (110) surface of n-GJTe
 $V_i = 0.86\text{eV}$; $N_d = 1.7 \times 10^{17} \text{ cm}^{-3}$; $\phi_p = 0.93\text{eV}$.

diodes however exhibited barriers of height around 0.93eV. An XPS deposition profile is shown in fig. 1.22. This shows that as the Al is laid down so the emissions due to Cd and Te both diminish at a roughly equivalent rate. This behaviour is different to the behaviour patterns identified for Al on vacuum cleaved surfaces. The relevance of this to the differences in Schottky barrier heights will be discussed later. LEED showed the Al overlayer to be polycrystalline.

(d) COPPER (Cu)

I - V and C - V measurements produced conflicting results. I - V measurements produced barriers of 0.53eV to 0.65eV with n values ranging from 1.01 to 1.2. Rectification at a bias of 0.5V was typically 10^2 to 3×10^2 . C - V however produced fairly linear C^{-2} versus V plots yielding barriers ranging from 0.60eV to 0.69eV.

(e) INDIUM (In)

Indium on air cleaved CdTe produced good agreement between I - V and C - V measurements. I - V typically produced barriers of height 0.51eV to 0.55eV with n in the range 1.7 to 1.9. C - V measurements produced fairly linear C^{-2} versus V plots yielding barriers of height 0.52eV to 0.57eV.

(f) TIN (Sn)

Tin on air cleaved CdTe produced barriers as measured by I - V techniques of ~0.60eV with n values 1.4 to 1.6 typically. C - V measurements produced barrier heights of

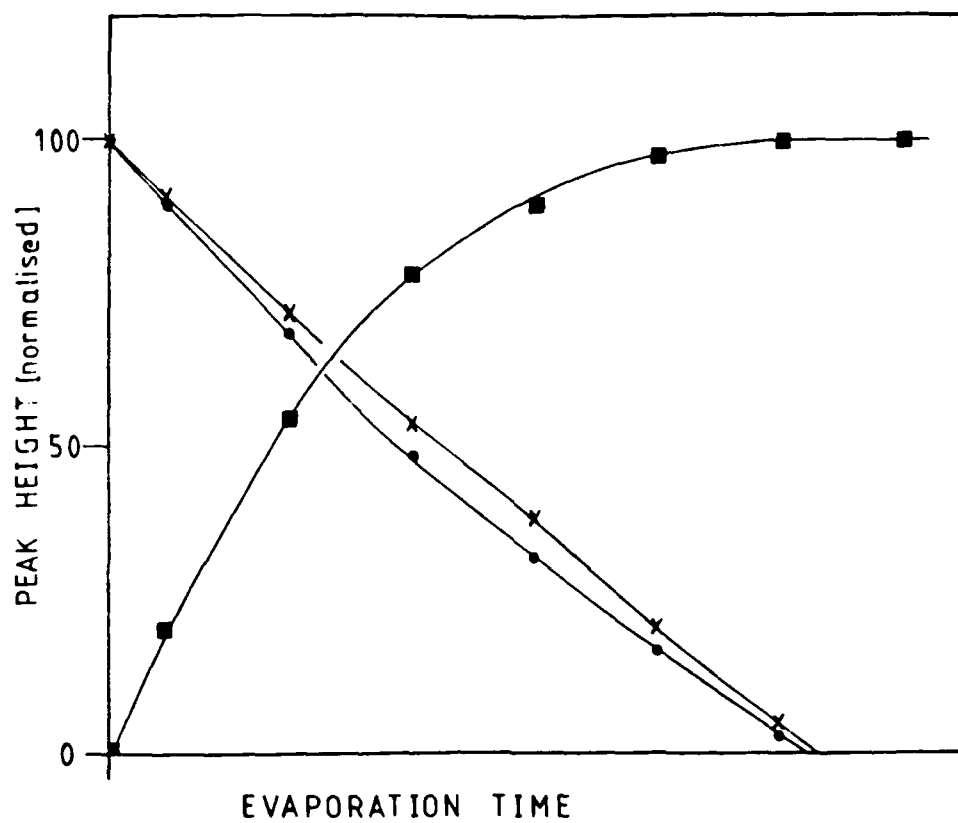


Fig. 1:22 : Deposition profile of Al depositing onto an air cleaved (110) surface of n-CdTe as measured by XPS.

■ = Al; ● = Te; X = Cd.

~0.58eV to .64eV with fairly linear C^{-2} versus V plots.

(g) NICKEL (Ni)

I - V measurements of Ni-air cleaved CdTe interfaces yielded barrier heights of 0.55eV to 0.65eV with n values typically 1.02 to 1.2. Rectification, at 0.5V, was typically $10^2 - 10^3$. C - V measurements produced barriers of 0.55eV to 0.65eV with linear C^{-2} versus V plots. An XPS deposition profile is shown in fig. 1.23. Initially both Cd and Te emissions reduce at roughly the same rate. At higher Ni coverage, however, one sees the Cd emission reaching a point of stability while the Te emissions continue to diminish. At high coverage of Ni ($>50\text{\AA}$) both Te and Cd emissions are seen in the metal overlayer indicating considerable intermixing of the CdTe, oxide and Ni species.

(h) PLATINUM (Pt)

I - V and C - V measurements on Pt-air cleaved CdTe interfaces yielded barriers greater than 1eV. I - V produced barriers in the range 1.01eV to 1.1eV with high n values of 1.2 to 1.7. Rectification at 0.5V was $\sim 10^3$. C - V produced fairly linear $1/C^2$ versus V plots yielding barriers of height 1.29 to 1.33eV.

(i) Summary of Results of Various Metals on Air Cleaved CdTe

From the results presented above it is clear that the introduction of an oxide layer between the metal contact and the clean CdTe has severely modified the Schottky barrier behaviour. For all metals studied the Schottky barriers are increased when an oxide layer is present between the clean

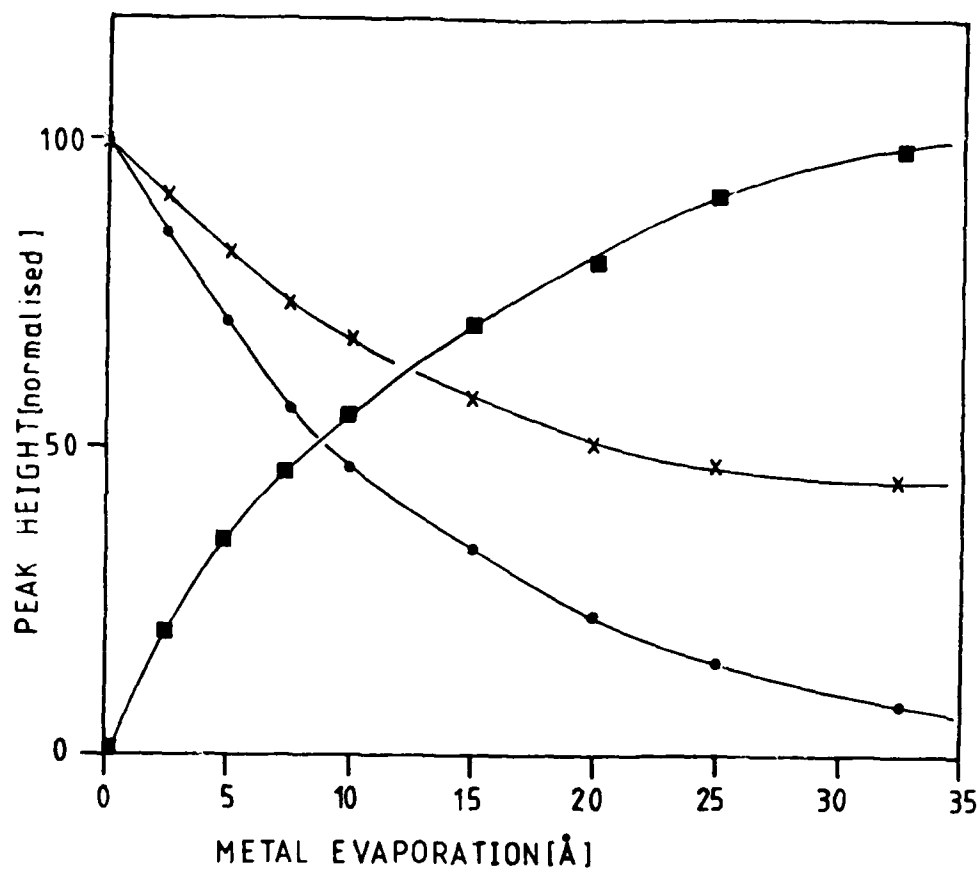


Fig. 1:23 : Deposition profile of Ni depositing onto an air cleaved (110) surface of n-CdTe as measured by XPS.

■ = Ni; ● = Te; X = Cd.

CdTe surface and the deposited metals. However the increases in Schottky barrier heights are not all of the same magnitude. The barrier heights for the various metal-vacuum cleaved surface and the various metal air cleaved surface are presented in table 1.2.

From table 1.2 it is immediately obvious that the use of an interlayer between the metal and semiconductor has a marked effect on the Schottky barrier behaviour. It is of interest then to speculate about using interlayers between the metal and semiconductor to control the Schottky barrier height. To this end we have used interlayers of variable thickness to modify the Schottky barrier. However as it is not really possible to accurately measure oxide thicknesses during formation it was decided to use interlayers of the reactive metal Al between vacuum cleaved surfaces of CdTe and Au contacts. Al was chosen because thick Al films on vacuum cleaved CdTe produce ohmic contacts, Au was chosen as it produces consistently high Schottky barriers of $\sim 0.96\text{eV}$. The results of these investigations are presented below:

1.2:(iii) The Use of Reactive Interlayers of Al between the CdTe Surface and the Au contact

Fig. 1.24 shows the I - V characteristics of diodes prepared with various Al interlayer thicknesses. The thickness of the Al interlayer was varied from 0\AA to 5\AA of Al. However the results shown here are for the interlayer thicknesses 0.8\AA and 2\AA . Also shown for comparison are the I - V characteristics of an Al-vacuum cleaved CdTe diode and a Au-vacuum cleaved CdTe diode. This diagram shows that by having as little as 2\AA of Al between the vacuum cleaved

Metal	$\phi_{B.a.c.}$ (eV)		Typical $\phi_{B.a.c.}$	Typical $\phi_{B.v.c.}$		$(\phi_{B.a.c.}-\phi_{B.v.c.})$ (eV)
	I-V	C-V		(eV)	(eV)	
Au	0.98-1.1	1.0 -1.15	1.1	0.96		0.14
Ag	0.50-0.57	0.53-0.55	0.53	ohmic		0.53
Al	0.90-0.93	0.92-1.0	0.93	ohmic		0.93
In	0.51-0.55	0.52-0.57	0.52	ohmic		0.52
Sn	0.60	0.58-0.64	0.60	0.40		0.20
Cu	0.53-0.65	0.60-0.69	0.60	0.45		0.15
Ni	0.55-0.65	0.55-0.65	0.63	0.40		0.23

Table 1.2: Barrier heights measured for the metal-air cleaved CdTe interfaces ($\phi_{B.a.c.}$). For comparison typical values of barrier height for the same metals on the vacuum cleaved CdTe surface are presented ($\phi_{B.v.c.}$).

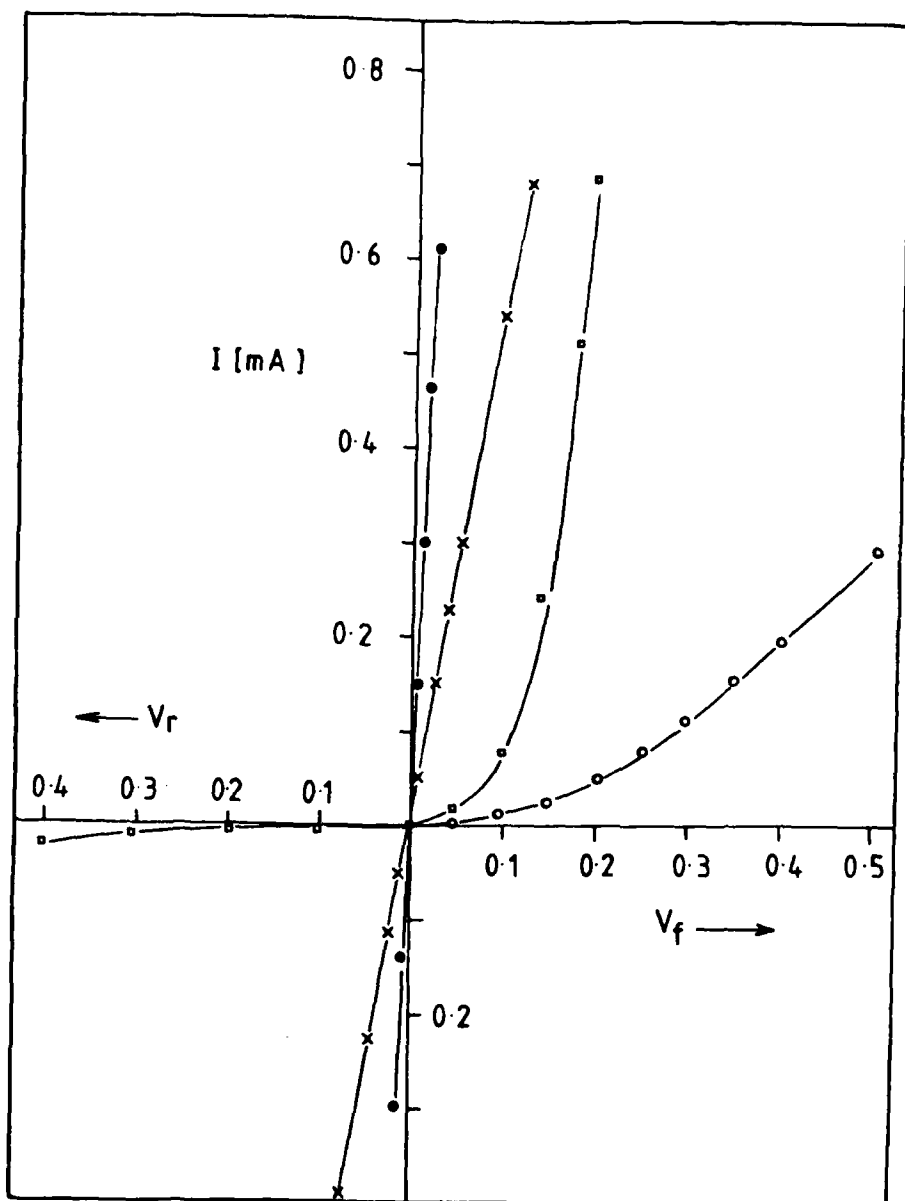


Fig. 1:24 : Current-voltage characteristics (d.c.) for various metal contacts to the vacuum cleaved (110) surface of n-CdTe.
 \bullet = Ag ; \times = 2Å Ag-Au ; \square = 0.8Å Ag/Au ; \circ = Au.

(110) surface of CdTe and the Au contact, the Schottky barrier behaviour has been drastically changed from a barrier of 0.96eV to an ohmic or very low barrier contact. At lower Al interlayer thickness, 0.8\AA , one still sees an appreciable Schottky barrier although the I - V value of barrier height is reduced from the barrier height of a simple Au-vacuum cleaved CdTe diode to 0.62eV.

1:3 DISCUSSION

The above results indicate that, in general, good agreement between Schottky barrier heights as measured by the traditional I - V and C - V techniques and by the band bending observed by UPS has been achieved for the metal-vacuum cleaved CdTe systems. It has been shown that the type of Schottky barrier behaviour observed on CdTe is very dependant on both the metal and on the nature of the CdTe surface. It has been shown that for many of the metal-CdTe interface systems examined the interfaces are not abrupt with interface widths in some cases, being wide. It has been shown that the CdTe surface is particularly unstable with respect to electron beams. When LEED, with a primary beam current of less than 1×10^{-6} A at ~ 100 V, is used the diffraction features are only visible for a short period of time. After this period of time, which may only be 30s, the LEED features become invisible in a rapidly growing diffuse background. The disordering caused by the electron beam used in AES has been shown to lead to a considerable shift of the Fermi level at the CdTe surface, pinning it, for an n-type crystal, in the lower part of the band gap. This shift has been measured at up to 0.6eV. The most likely reason for this disordering is localised electron beam induced heating of the CdTe surface on account of the extremely low thermal conductivity of CdTe ($0.058 \text{ W.cm}^{-1}\text{deg}^{-1}$ at 32.7°C)⁴. This immediately gives rise to the problem of studying ordered surfaces of low thermal conductivity using incident electron techniques, and goes some way to explaining the differences seen in deposition profiles of the formation of various metal-CdTe interfaces as monitored by AES and XPS. The validity of the assumption that, for CdTe, XPS deposition

profiles more truly reflected the formation picture than AES is confirmed.

It has become evident that one of the main differences between the behaviour of metals on vacuum cleaved CdTe and other semiconductor compounds is on the rate of the development of the Schottky barrier. If one compares the formation of gold contacts to CdTe and the III - V compound GaAs this difference in behaviour is illustrated. For GaAs the Schottky barrier is largely formed at a coverage of 20% of a monolayer⁵. For CdTe this is certainly not the case and much higher metal coverages are needed to produce the maximum shift in the Fermi level at the surface.

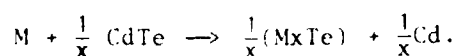
From the results presented above on metal vacuum cleaved CdTe systems it is clear that the interfaces are not atomically abrupt and that in some cases interface widths can be considerable, an observation that was made for the related II - VI compounds CdS and CdSe by Brucker and Brillson⁶. As such the relevance of theories to this system which assume that interfaces between the metals and semiconductor surfaces are abrupt must be in question.

Chemical processes that occur at these interfaces must play a role in the ultimate determination of the Schottky barrier behaviour. The results have shown that different metals produce different deposition profiles. So it will be of considerable interest to consider the role played by chemical effects at these interfaces.

Brillson⁷ noticed a relationship between the heat of reaction (ΔH_R) of a metal with the semiconductor material and the Schottky barrier height for a range of systems.

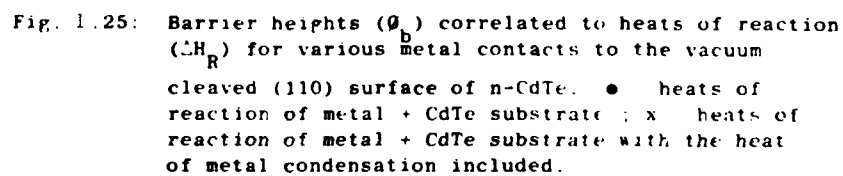
A critical

heat of reaction, ΔH_{RC} , appears to exist in each system at which a transition from a region of low Schottky barrier behaviour to higher Schottky barrier behaviour occurs. In figure 1.25 the heat of reaction of various metals with CdTe is plotted against the Schottky barrier height. The heats of reaction are determined from the reaction:



from the heats of formation (ΔH_f) values of the compound semiconductor CdTe and the most stable metal telluride product⁸. These values of ΔH_R are normalised per metal atom analogous to the ΔH_R calculations of Andrews and Phillips⁹. From fig. 1.25 it does appear that those metals with high heats of reaction (greater than 0.3eV metal atom⁻¹) lead to Schottky barriers. Those metals with heats of reaction less than this figure give very low barrier or ohmic behaviour. If however one takes into account the heat of condensation¹⁰ of the metal and introduces this to the equation determining the heat of reaction then the apparently simple relationship between ϕ_b and ΔH_R disappears. The heats of reaction, for the various metal CdTe systems, with and without metal condensation effects are presented in table 1.3. However it is not really clear just how meaningful the heat of condensation is in these systems as the results, particularly UPS and XPS has indicated that in many cases the metal does not simply condense into a metallic overlayer on impinging on the CdTe surface. Some e.g. In, Al may indiffuse while in other systems Cd outdiffuses into the forming metallic overlayer thus complicating the calculations.

More recently Brillson¹¹ has shown that for the III - V



Metal	ΔH_R (eV. metal atom ⁻¹)	ΔH_R^* (eV. metal atom ⁻¹)
Au	+1.93	-1.88
Ag	+0.29	-2.67
Al	-0.25	-3.67
In	-0.04	-2.56
Sn	+0.33	-2.81
Cu	+0.59	-2.91
Ni	+0.40	-4.1

Table 1.3: Heats of reaction (ΔH_R) of various metals with CdTe to form the most stable tellurides. Heats of formation of the various telluride compounds are taken from reference 8. Also presented are the heats of reaction of gaseous metals condensing on the CdTe surface and then reacting to form the most stable telluride (ΔH_R^*). Heats of condensation are taken from reference 10.

compound semiconductors that the most reactive metals, those with negative heats of reaction, form the most abrupt interfaces, whereas those with positive heats of reaction produce interface widths many angstroms wide. As most of the metals investigated by us on CdTe have positive heats of reaction, the exceptions being In and Al which have slightly negative heats of reaction, then the fact that the interfaces between the metals and the CdTe are not abrupt is consistent with Brillson's observations.

For metals on vacuum cleaved CdTe the results can be evaluated and summarised as follows. For low work function metals ($\phi_m < 4.3\text{eV}$) the Schottky barrier height is less than 0.1eV regardless of whether there is Cd outdiffusion onto the metal contact. For metals of larger work function, with the exception of Ni, the Schottky barriers formed are in rough accordance with the linear interface potential model in the Schottky limit¹². As was indicated previously, in many studies of metal semiconductor systems workers have attempted to interpret the way in which S , the index of interface behaviour varies from one metal semiconductor system to another and in particular the sharp transition in values of S , which seems to be near to zero for metals on covalent semiconductors and close to unity for metals on ionic semiconductors. S is obtained from the dependance of barrier height, ϕ_b on the metal work function ϕ_m using a relationship of the form¹³.

$$\phi_b = S(\phi_m - \phi_{sc}) + C$$

Kurtinet al.¹³ and later Schluter¹², in surveys of the various systems report a value of S for CdTe of ~ 0.2 .

This is a somewhat surprising value in view of the ionic nature of CdTe. As table 1.1 and fig.1.26 show, the barrier heights on vacuum cleaved CdTe surfaces shows a relatively linear dependence on the metal work function. The exception being the Ni - CdTe system which will be discussed below. If as has been reported^{12,13} the value of S for CdTe is low at ~ 0.2 then one would expect very little scaling of ϕ_b with ϕ_m . The results here show that, with the exception of the Ni-vacuum cleaved CdTe system, metal-vacuum cleaved CdTe systems do adhere relatively well to the Schottky model of Schottky barrier behaviour with a value of S , the index of interface behaviour close to unity. The Ni-CdTe system is not consistent with this behaviour, as fig. 1.26 shows. Here the Fermi level at the surface appears pinned at $\sim 0.5\text{eV}$ below the conduction band, an observation which suggests that a combination of cadmium outdiffusion and a high work function metal leads to the presence of states at the interface which effectively prevent the Fermi level at the semiconductor surface from shifting further than $\sim 0.5\text{eV}$ below the conduction band edge. It is of interest to question the nature of the defects which could cause these states to be present. It has been suggested that for the metal III - V systems neutral anion and cation vacancies play an important role and that the resultant barriers can be related to an excess of anions or cations incorporated in the metal electrode. Clearly for several of the metal CdTe systems such types of defects do appear to exist. It is known that the defect structure of CdTe is complex¹⁴. Daw and Smith¹⁵ have calculated, using a tight binding approach, the defect levels due to simple neutral anion and cation vacancies on

the bulk and near the surface for a range of III - V and II - VI compound semiconductors. For the III - V semiconductors the calculated levels fall within the band gap and there seems to be a clear correlation between the resultant Fermi level pinning, Schottky barrier formation and the existence of these defects. For CdTe however it seems that the corresponding levels fall well outside the band gap and as such may be ineffective in pinning the Fermi level near the interface and thus in influencing the Schottky barrier formation. If however the vacancies are considered to be charged species rather than neutral ones a different result may ensue. Several acceptor levels have been observed in the band gap of bulk CdTe and the assignment of causative species to these levels have been many. Comprehensive lists of these appear in articles by Kroger¹⁶ and more recently by Takebe et al.¹⁷. The levels within the band gap which are believed to be correctly assigned to charged Cd vacancies are at $E_C - 0.6\text{eV}$ to $E_C - 0.7\text{eV}$ for a doubly charged Cd vacancy and at $E_V + 0.05\text{eV}$ to $E_V + 0.06\text{eV}$ for a singly charged vacancy. If one postulated that for the case of the Ni-CdTe system the Cd outdiffusion led to the presence of, in a large enough concentration of, doubly charged Cd vacancies at the semiconductor interface then the resultant pinning of the Fermi level would produce the Schottky barrier behaviour seen. Even though Cd outdiffusion occurs at other metal-CdTe interfaces e.g. Al, Cu where the metal work function is low the resulting energy levels generated do not influence the Fermi level position. It is of some interest to consider these postulations in the light of recent work by Kuech¹⁸. In this work the importance of Cd

defects at the metal-CdTe interface was recognised. He found that the use of Cd/Au alloys markedly affected the barrier behaviour seen.

Introduction of oxide layers between the metal contact and the clean CdTe surface modifies the Schottky barrier behaviour. Oxidation of the CdTe surface by exposure to air at atmospheric pressure for 48 hours produces a TeO_2 layer on the surface²⁶.

For all systems investigated the presence of this oxide layer between the metal and the semiconductor surface leads to increases in Schottky barrier heights (see fig. 1.26). It should be noted however that the increases are not all of the same magnitude. It is possible that several processes may contribute to this. Firstly, disruption of the CdTe surface by the oxidation process may give rise to some surface states within the band gap thus affecting the Fermi level at the semiconductor surface. Secondly impinging metal atoms may react chemically with the surface TeO_2 to form metal oxide layers which may lead to a change in work function of the overlayer. The heats of reaction of the various metals used with TeO_2 to form the stable metal oxides have been calculated and are presented in table 1.4. These show that reactions between metals and the TeO_2 are energetically favourable for the metals Al, In, Cu, Sn and Ni. For some of these metals it has been documented that changes in work function do occur when the metals are oxidised. In 1960 Van Laar & Scheer¹⁹ reported that exposure of indium metal to air at atmospheric pressure increases the work function from $\sim 4.1\text{eV}$ to $\sim 4.6\text{eV}$. In 1960 Anderson & Klemperer²⁰ reported that the work function of outgassed Ni was $\sim 5.1\text{eV}$ but the work function of

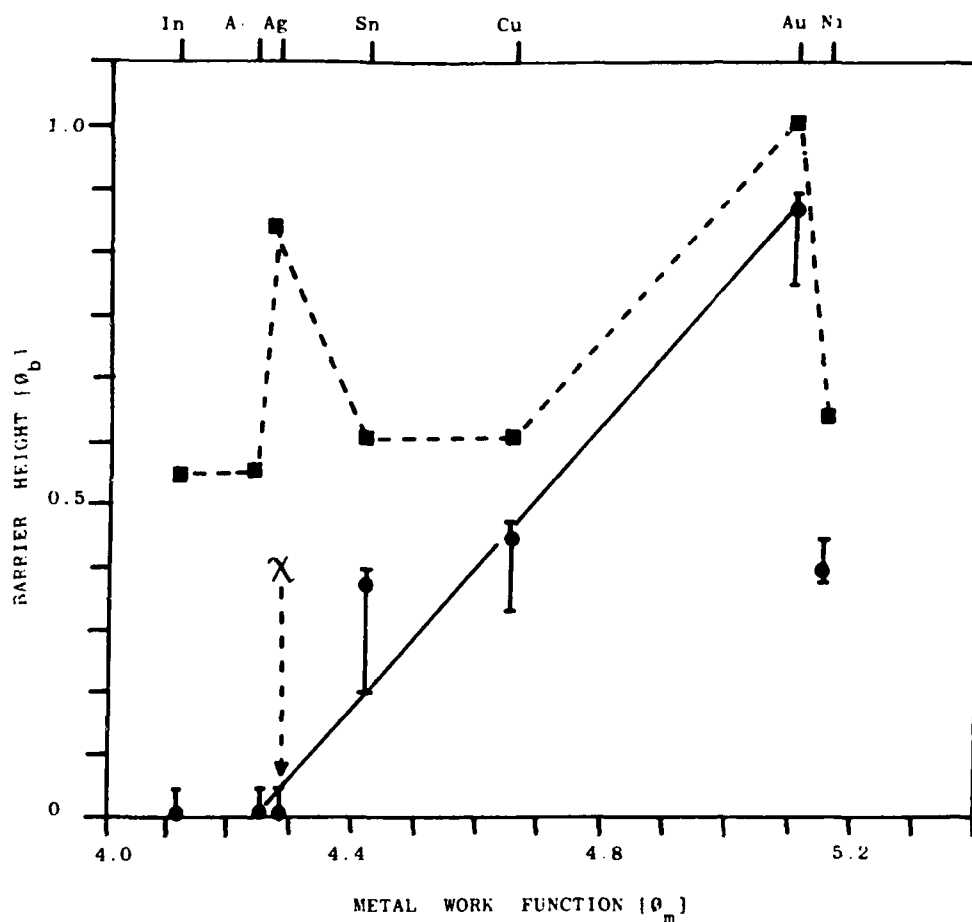


Fig. 1.26: Plot of barrier height (ϕ_b) versus metal work function (ϕ_m) for various metal-vacuum cleaved (110) CdTe interfaces and for various metal-air cleaved (110) CdTe interfaces. Data is taken from table 6.2. \bullet is the typical barrier height for the vacuum cleaved surface; \blacksquare is the typical barrier height for the air cleaved surface. The bars associated with the vacuum cleaved surface barrier heights show the range of barrier heights measured by the methods of I-V, C-V and UPS. The electron affinity of CdTe (χ) is indicated on the plot

Metal	Most stable oxide	ΔH_R (eV. metal atom ⁻¹)
Au	Au ₂ O ₃	+1.58
Ag	Ag ₂ O	+1.35
Al	Al ₂ O ₃	-12.32
In	In ₂ O ₃	-4.6
Sn	SnO ₂	-2.68
Cu	Cu ₂ O	-0.08
Ni	NiO	-1.63

Table 1.4: Heats of reaction (ΔH_R) of various metals with TeO₂, present on the air cleaved surface of CdTe, to form the most stable oxides. Heats of formation of the various oxides are taken from reference 8.

outgassed NiO was $\sim 5.5\text{eV}$. However more recently Benndorf et al.²¹ (1980) have suggested that exposure of clean Ni (110) to oxygen resulted in island growth of NiO with a resulting decrease in work function. Hence it is difficult to know exactly what work functions to consider for the overlayers on metal-air cleaved CdTe systems.

Recently Brucker and Brillson²² have investigated metal-CdS and metal-CdSe systems where ultra thin layers of Al have been deposited between the semiconductor and the Schottky contact (Au). They found that by varying the thickness of the Al interlayer that appreciable modification of the Schottky barrier height could be achieved. Al and Au were chosen as metal contacts as they produce limiting behaviour in terms of barrier height for CdS and CdSe i.e. Al yields ohmic contacts and Au yields close to maximum barriers^{22,23}. They concluded that the observed modification in Schottky barrier height was dependent on the density of metal induced surface states rather than a qualitative change in the nature of these states. The results presented in chapter 1:2:(iii) show a similar pattern of behaviour to those seen by Brucker and Brillson on CdS and CdSe. So the question must then be asked as to whether a similar philosophy can be applied to the results observed here for thin interlayers of Al between the CdTe and Au contact. It is known that Al can act as a shallow donor at $E_c - 0.014\text{eV}$ in bulk n-type CdTe, so that near surface doping by incident Al atoms could generate similar states at the interface. If the density of these states is large enough then a highly n-type surface layer of CdTe may ensue with the Fermi level being located very near to the conduction band edge.

The UPS measurements taken during the formation of an Al-vacuum cleaved CdTe contact have shown that a movement of the Fermi level at the surface towards the conduction band is indeed seen for very small coverages of Al, prior to any evidence of metallic Al being seen on the surface. If at this point in the Al metal deposition procedure we now deposit instead a thick Au overlayer then charge transfer to the Au would occur. The result being a Schottky barrier of effective height lower than that for the simple Au-vacuum cleaved CdTe system, as a result of tunnelling through the resulting very thin region of the so formed barrier. This type of result is seen for an Al interlayer thickness of 0.8\AA . An increase of this interlayer thickness to 2\AA produces contacts ohmic in nature. The result would indicate that one now had a metallic Al overlayer on the CdTe surface. Although the Fermi level at the surface has moved nearer to the conduction band due to the indiffused Al atoms acting as shallow donors one now has charge transfer occurring between the semiconductor and the metallic Al overlayer rather than the subsequently deposited Au. The result being a contact essentially identical to a thick film Al-vacuum cleaved CdTe contact i.e. ohmic in nature.

One must also consider the possibility of the formation of "islands" of Al on the CdTe surface at very low coverages. Deposition of an Au electrode on top of this would result in an electrical contact of "mixed phases" where different Fermi level pinning behaviour occurs. Recently, Freeouf et al²⁴ have carried out a theoretical analysis of "mixed phase" contacts. They showed that where a contact exists in which there are phases showing differing Fermi level pinning

behaviour then interactive effects are such that in measuring the contact characteristics one would only see one averaged Fermi level position. If for the contact with 0.8\AA of Al it is postulated that at this coverage one achieves islands of Al on the CdTe surface then subsequent Au deposition will lead to a mixed phase contact. The electrical properties of which can be understood as being consistent with the Fermi level averaging concept. With 2\AA of Al between the CdTe and the Au the situation is different. It is now assumed that the Al islands or patches have developed into a smooth continuous film of atomic thicknesses. If 2\AA of Al form such a film on CdTe then even with subsequent deposition of Au on top of such a film one still has simply a single phase contact with only one Fermi level pinning behaviour in evidence. The result is a very low barrier or ohmic contact.

1:4 CONCLUSIONS

It has been shown that interfaces formed between various metals and the vacuum cleaved (110) surface of CdTe are not abrupt, with interface widths spreading over, in some cases, many tens of angstroms. Our LEED investigations have shown that for all metals studied on vacuum cleaved CdTe the metal overlayers develop as polycrystalline rather than crystalline layers. Various metals produce various chemistries at the interface yet if one eliminates the cases where Cd outdiffusion occurs into high work function metal overlayers, i.e. the Ni-CdTe system then the data adheres closely to the linear interfacial model in the Schottky limit. For these metals the value of S , the index of interface behaviour, is much closer to unity than previously reported. The reasons for the nonadherence to the linear interfacial model in the Schottky limit of high work function metals where Cd outdiffusion occurs is undoubtedly linked to the creation, within the band gap, of pinning levels due to doubly charged Cd vacancies which effectively pin the Fermi level at $\sim 0.6\text{eV}$ to 0.7eV below the conduction band. For lower work function metals where Cd outdiffusion occurs into the metal overlayer, Al and Cu, the resultant levels created in the gap by the Cd vacancies do not affect the Fermi level movement.

The introduction of reactive interlayers between the CdTe and the metal overlayer changes the situation radically. Oxide layers on the CdTe surface, produced by cleaving in air, lead to increases in Schottky barrier height for all metals studied. More complex behaviour patterns during deposition are seen. In fact such is the complexity of these

systems that much more data will be required before the dominant mechanisms responsible for the Schottky barrier formation at these metal-air cleaved CdTe interfaces.

Use of Al interlayers between the CdTe and the Au contact produces effects which may be understood as being caused by one of or both of two mechanisms. Either indiffusion of Al into the CdTe with a resulting barrier reduction or the formation of islands of Al at low Al coverage resulting in "mixed phase" contacts which produce an averaged Schottky barrier height.

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Appendix to Section 1:

Publications resulting from the work presented in Section 1.

Schottky barriers at metal-CdTe interfaces

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We have adopted the multitechnique approach to investigate the Schottky barrier formation for a range of metals on clean cleaved (110) surfaces of cadmium telluride. We have probed the growth of tin, nickel and copper films on these surfaces by XPS, UPS, LEED and AES. Thick film values of Schottky barrier height were established by C-V and I-V techniques, and confirmed by monitoring the degree of band bending observed by UPS. The results are discussed together with those already reported for Au, Ag and Al on CdTe. The results indicate that in many cases the interfaces formed are not abrupt and that intermixing between the metal and the CdTe occurs. The observations are discussed in terms of the various theories of Schottky barrier formation. In particular the role of the metal atoms as possible dopants, the role of the heats of reaction of the metal with the CdTe surface, the relevance of the metal work function and the applicability of the defect model to the metal-CdTe system are discussed.

Introduction

The mechanism responsible for the formation of Schottky barriers at the interface between metals and semiconductors has been the subject of much research over the past years. Several elegant theories¹⁻⁶ have been put forward to account for the Schottky barrier formation, but to date there has been little agreement as to the most important processes involved. These theories have considered the relevance of intrinsic surface states on the semiconductor^{1,2}, the tunnelling of metal wave functions into the semiconductor^{3,4}, many body effects⁵, and metal induced gap states⁶. In general, though, all these theories make the assumption that the interface formed between the metal and the clean semiconductor is both ordered and atomically abrupt. Recently, however, it has been shown that this assumption is not universally correct^{7,8}, and that in many cases considerable intermixing of the metal and semiconductor occurs even for interfaces fabricated at room temperature. It has recently been established that defects, such as cation or anion vacancies, caused by this intermixing at the interface can dominate the formation of the Schottky barrier⁹⁻¹¹. The interfaces formed between metals and the III-V compound semiconductors have been extensively investigated and it has been found that some metals, such as aluminium, can disrupt the semiconductor surface by chemically reacting with it¹². Other workers have shown that considerable intermixing of the metal and semiconductor for the Au-GaSb system occurs even at room temperature⁹. It has also been shown that exposure of a clean semiconductor surface to an atmosphere, such as O₂, prior to metal evaporation can cause a change in the transport properties of the metal-semiconductor interface, in some cases as a result of doping the surface layers of the semiconductor^{12,13}. As a result of these investigations it is now becoming generally accepted that the formation of Schottky barriers on the III-V

compound semiconductor is often dominated by the nature of the metal or near the surface of the semiconductor.

To find out how applicable the defect model is to other metal-semiconductor systems, we have extended our investigations to a metal-III-V semiconductor system. In this paper we report on the fabrication of metal contacts to cadmium telluride. Initial studies of Au, Ag and Al film growth on vacuum cleaved CdTe have already been described elsewhere¹⁴.

Experimental

Cadmium telluride crystals, doped with indium, with carrier concentrations in the range 10^{16} – 10^{17} cm⁻³ were grown at our laboratory by a vertical Bridgman technique. Our method of experimentation involves carrying out complementary surface investigations sequentially on the same sample in the same ultra-high vacuum chamber without breaking the vacuum. To enable us to do this we have three uhv chambers at our disposal. One contains the techniques of X-ray photoelectron spectroscopy (XPS), Auger electron Spectroscopy (AES) and Low energy electron diffraction (LEED). The second uhv chamber contains facilities for XPS, LEED and uv photoelectron spectroscopy (UPS). The third uhv chamber contains AES, LEED and the facility to carry out I-V and C-V measurements.

After mounting the crystals in suitable holders, the crystals could be cleaved to produce atomically clean (110) surfaces in a vacuum of $\sim 10^{-10}$ torr.

Our approach is first of all to characterize thoroughly the vacuum cleaved (110) surface of CdTe by the techniques available to us. Controlled amounts of metal, from fractions of a monolayer upwards are evaporated onto the clean surface of CdTe. The early stages of Schottky barrier formation are then monitored by XPS,

UPS and AES. Once a thick overlayer of metal had been established the Schottky barrier heights were measured, in part, by conventional I-V and C-V techniques. At this stage LEED was carried out to determine the degree of order present in the metal overlayer. The results presented are for experiments carried out at room temperatures.

Results

In this paper we summarize the results obtained for the evaporation of various metals on vacuum cleaved CdTe. The general approach is typified by the results for Cu. Figure 1(a) shows the UPS spectra measured for vacuum cleaved CdTe with progressive deposition of copper onto the surface. Spectra are measured in the angle resolved mode along the surface normal. The various peaks observed in the clean spectrum may be understood to a first approximation in terms of bulk electron states.⁴ The two close peaks prominent at a binding energy of 10.9 and 11.5 eV originate in the spin-orbit split Cd4d levels.

As copper is deposited on the clean surface all levels in the photoemission spectrum appear to shift to lower binding energies. This is due to the fact that the Fermi level at the surface is shifted towards the valence band by 0.2 eV, as illustrated in Figure 1(a) (inset). This interpretation assumes that the bands near the atomically clean surface are flat and that the electron escape depth (10–20 Å) is short compared to the band bending (several hundred Å) following metal deposition. The Schottky barrier measured by I-V methods following the deposition of a thick Cu film was 0.4 eV which is entirely consistent with the Fermi level shift shown in Figure 1(a).

Another noticeable feature in the spectra is the gradual appearance of a small peak at a binding energy of ~10.3 eV, i.e. at an energy of ~0.6 eV less than that of the Cd4d levels in CdTe, as Cu is progressively deposited. This peak is due to cadmium atoms which are in a different environment to those cadmium atoms in the CdTe, i.e. due to cadmium incorporated in the copper overlayer. Unfortunately the possible out-diffusion of tellurium is difficult to assess by UPS since no core levels are accessible. However XPS studies lead to the conclusion that both Cd and Te are incorporated in the Cu electrode and that the interface is very far from being atomically abrupt and extends over many tens of angstroms.

Finally LEED observations of the thick metal overlayer indicate polycrystalline film growth for all metals studied. Nickel behaved in a very similar manner again leading to a non abrupt interface and a Schottky barrier height of 0.45 eV (see Table 1). Gold led to a much higher Schottky barrier, with UPS behaviour

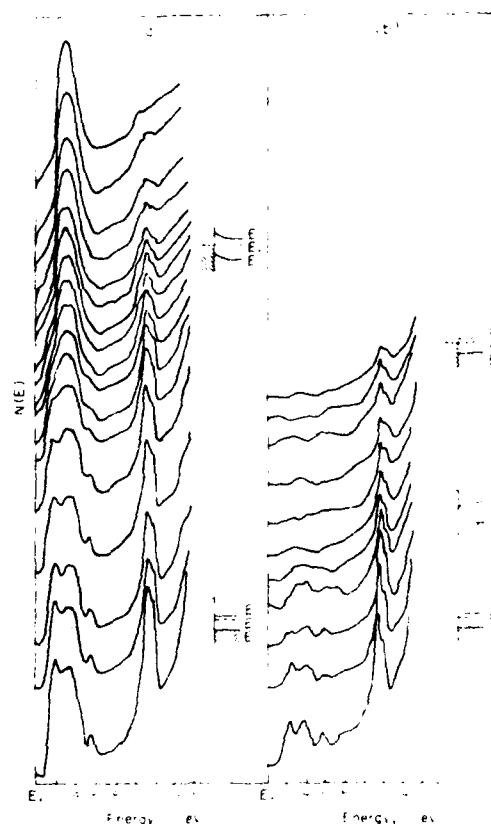


Figure 1. (a) Angle-resolved photoelectron spectra for vacuum cleaved CdTe with controlled evaporation of copper. Spectra shown are for normal emission, $h\nu = 21.2$ eV, angle of incidence of light = 55° . The insets show the position of the valence and conduction bands with respect to the Fermi level. (b) Angle-resolved photoelectron spectra for vacuum cleaved CdTe with controlled evaporation of indium. Spectra shown are for normal emission, $h\nu = 21.2$ eV, angle of incidence of light = 55° . The insets show the position of the valence and conduction bands with respect to the Fermi level.

similar to Cu and Ni, but no evidence of Cd in a different chemical environment to that in CdTe was found. For silver contacts on

Table 1. Barrier height measurements (ϕ_b), Schottky theory predictions ($\phi_{st} = Z_{eff}/r$), heats of reaction of various metals with CdTe. (the heat of reaction value ΔH_r^0 includes an allowance for the heat of condensation of the metal²⁰)

Metal	Barrier heights		ϕ_m^{28} (eV)	$(\phi_m - Z_{eff}/r)$ (eV)	ΔH_r (eV metal atom ⁻¹)	ΔH_r^0 (eV metal atom ⁻¹)
	I-V	UPS				
Au	0.92	0.85	5.1	0.82	-	-
Al	Ohmic	Ohmic	4.26	< 0	-0.25	-3.67
Ag	Ohmic	Ohmic	4.28	0	+0.29	-2.67
In	Ohmic	Ohmic	4.12	< 0	-0.04	-2.56
Sn	< 0.4	0.3	4.42	0.14	-0.33	-2.81
Cu	< 0.4	0.2	4.65	0.37	+0.59	-2.91
Ni	< 0.45	0.4	5.15	0.8*	+0.40	-4.1

clean CdTe (110) surfaces no Fermi level movement was observed and indeed the I-V measurements showed largely ohmic behaviour consistent with a very low barrier. Again, like Au, no evidence of Cd in a different chemical environment to that in CdTe was found.

The results obtained for the three metals In, Al and Sn showed noticeable and important differences in behaviour from those illustrated by Figure 1(a). Following the deposition of small fractions of a monolayer of In, for example, the whole photoemission spectrum, originating in the bulk CdTe, displays a shift to higher binding energy. Figure 1(b), indicative of a shift of the Fermi level towards the conduction band by ~ 0.2 eV [see inset of Figure 1(b)]. As the metal overlayer grows into a continuous film the spectra experience a shift back to the original binding energies. Similar effects were observed for Al. In also showed similar behaviour except that the final Fermi level position is about 0.2 eV closer to the valence band at the surface as compared to the flat band condition (see Table 1). In all three cases electrical measurements showed barrier behaviour consistent with these interface Fermi level positions. For these three interfaces XPS studies showed evidence of considerable intermixing.

The instability of the vacuum cleaved (110) surface of CdTe was demonstrated when the same investigation of the interface chemistry was carried out using the technique of Auger electron spectroscopy. The results proved to be inconsistent and occasionally contradicted the behaviour shown up by XPS. An example of this is shown in Figure 2 where the formation of an aluminium electrode is monitored by both AES and XPS. It is obvious that the interface mixing process is being influenced by the incident electron beam. The disorder introduced by the electron beam may be due, at least partially, to localized heating of the surface as a result of the very low thermal conductivity of the CdTe ($0.058 \text{ W cm}^{-1} \text{ deg}^{-1}$ at 32.7°C^{15}). This disorder can lead to a considerable shift in the Fermi level at the surface of the crystal pinning it in the lower part of the band gap. Using UPS we have noted⁸ that this shift can be as much as 0.6 eV. It must therefore be stressed that great care must be exercised in the

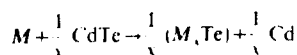
interpretation of data resulting from experimental techniques where electron beams are incident on the surface of the CdTe.

Discussion

Our results show that for CdTe there is very good general agreement between the Schottky barrier characteristics measured by C-V-I-V techniques and by UPS. One of the main differences between the behaviour of CdTe and other materials is in the rate of development of the Schottky barrier. If we compare the formation of gold contacts to CdTe and the III-V compound GaAs the difference in behaviour is illustrated. For GaAs the Schottky barrier is largely formed at a coverage of $\sim 20\%$ of a monolayer.¹² For CdTe this is certainly not the case and much higher metal coverages are needed to produce the maximum shift in the Fermi level at the surface.

From previous discussion it is clear that the metal-CdTe interfaces are not atomically abrupt. In fact of all the III-V and II-VI compounds studied by us CdTe has by far the most unstable surface. It is clear that electron beams disrupt the surface, as does the metal deposition itself. One problem that contributes to this effect is the low thermal conductivity of CdTe.

The formation of metal-CdS and metal-CdSe interfaces, both related II-VI materials, has been described by Brucker and Brillson¹¹. It was noted that, like CdTe, interfaces are not abrupt and that the interface widths can be considerable. Earlier Brillson¹¹ noticed a relationship between the heat of reaction (ΔH_R) of the metal with the semiconductor material and the Schottky barrier height (ϕ_b) for a range of systems. These heats of reaction are determined, for the reaction



from heats of formation (ΔH_f) values of the compound semiconductor CdTe and the most stable metal telluride product¹². These are normalized per metal atom, analogous to the ΔH_R calculations of Andrews and Phillips¹⁹. The heats of reaction of various metals with CdTe are tabulated in Table 1. From Brillson's results¹¹ it appears that there exists two definite regions of Schottky barrier behaviour. For unreactive metals one generally obtained high Schottky barriers, whereas reactive metals produced lower Schottky barrier behaviour. A sharp transition between these two types of behaviour occurred at a critical heat of reaction. For CdS and CdSe the critical heats of reaction are nearly identical at $\sim +0.5 \text{ eV metal atom}^{-1}$. In Figure 3 we plot ΔH_R against ϕ_b for various metals on CdTe. The value of ΔH_R for Au is not known, as the heat of formation of the stable gold telluride (AuTe₂) is not documented. From the results it does appear that those metals with high heats of reaction (greater than $0.30 \text{ eV metal atom}^{-1}$) lead to Schottky barriers. Those metals with heats of reaction less than this figure give very low or ohmic behaviour. If, however, one takes into account the heat of condensation²⁰ of the metal then the relationship between the heat of reaction and Schottky barrier height disappears. However it is not really clear how meaningful the heat of condensation is in these systems as the metal atoms are not simply forming metallic overlayers with abrupt interfaces on impinging on the CdTe surface. Brillson¹¹ has shown that the most reactive metals, those with negative heats of reaction, form the most abrupt interfaces. As most of the metals investigated by us, on CdTe, have positive heats of reaction, the exceptions being In and Al which have slight negative heats of reaction, then the fact that the interfaces between the metals and

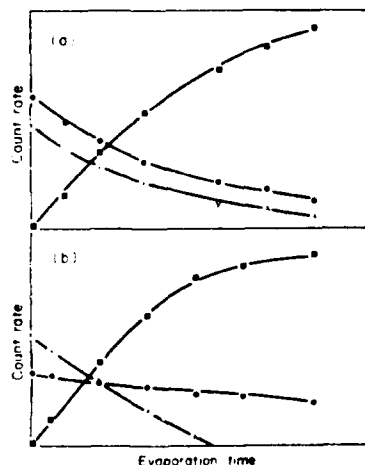


Figure 2. Deposition profiles of aluminum depositing on the vacuum-cleaved (110) face of CdTe as measured by (a) XPS, (b) AES. Key: \blacksquare —Al, \bullet —Te, \circ —Cd.

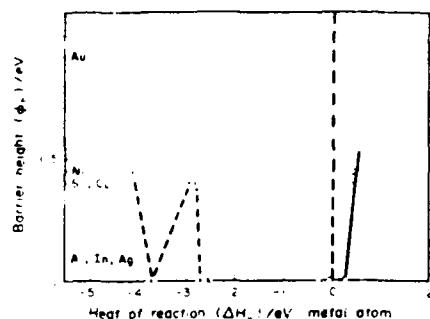


Figure 3. Barrier heights (ϕ_b) correlated to heats of reaction (ΔH_r) for various metals on CdTe. ϕ_b = Heats of reaction of metal + CdTe substrate. Heats of reaction of metal + CdTe substrate, with heat of metal condensation included.

the CdTe are not abrupt is consistent with the observations of Brillson on other II-VI compounds. It has also been suggested by Brillson that surface fields may lead to enhanced diffusion across these interfaces. In the metal/CdTe systems fields can be very high (up to 10^7 V cm $^{-1}$) and it is clear that these may have a significant effect on the diffusion. These ideas will be pursued in a later publication. In many of the theories which attempt to describe the basic physical processes responsible for Schottky barrier formation workers attempt to interpret the way in which the index of interface behaviour, S , varies from one metal/semiconductor system to another and in particular the sharp transition in values of S which seems to be near to zero for metals on covalent semiconductors and close to unity for metals on ionic semiconductors 22 . The quantity, S , is obtained from the dependence of ϕ_b on the metal work function, ϕ_m , using a relationship of the form 22

$$\phi_b = S(\phi_m - \phi_{sc}) + C$$

where ϕ_{sc} is the semiconductor work function and C is a constant. Kurtin *et al.* 22 and later Schluter 23 report that the value of S for CdTe is ~ 0.2 which is somewhat surprising in view of its ionic nature. It is clear that the values of barrier heights for various metals on CdTe correspond to a wide range of values. This is not consistent with a low value of S for CdTe as was previously suggested. This will be considered later.

It is of interest to probe the influence of defects in the metal/CdTe system. It has been suggested that for the metal/III-V systems, anion and cation vacancies play an important role and that the resultant Schottky barriers can be related to an excess of anions or cations incorporated in the metal electrode. Clearly for CdTe there appear to be defects at the interfaces but there does not seem to be any such simple relationship between the Schottky barrier behaviour and the excess of Cd or Te in the metal electrode as determined by XPS. It is known, however, that the defect structure in CdTe is complex. Daw and Smith 24 have calculated the defect levels due to simple neutral anion and cation vacancies in the bulk and near the surface of several III-V and II-VI compound semiconductors. The calculated levels fall within the band gap for the III-V materials and there seems a clear correlation between the Schottky barrier formation and the existence of these defects. For CdTe, however, it seems that the corresponding levels fall well outside the band gap and as such may be ineffective in pinning the Fermi level near the interface and thus in influencing the Schottky

barrier formation. Hence although in CdTe there are many defects at metal/CdTe interfaces they do not have such an influence on the Schottky barrier behaviour as is seen in metal/III-V systems.

In addition to out-diffusion of Cd and Te atoms there is also the possibility of in-diffusion of metal atoms and we must therefore consider the effect of these atoms as dopants of the surface layer. Doping of CdTe with In and Al can produce highly n -type material. In the bulk In and Al are known to act as shallow donors lying at 0.014 eV below the conduction band 25 . Au, Ag and Cu, however, produce deep acceptor levels, when introduced as dopants into bulk CdTe, at 0.3–0.4 eV above the valence band. Clearly if Au does form deep acceptors then this could explain the high Schottky barrier. It would then be surprising that Ag did not behave in a similar manner, if in-diffusion and doping were controlling the barriers. Hence it appears that there is no general relationship between the Schottky barrier and doping by the in-diffused metal atoms, although in individual cases, In, Al and Sn, doping effects may be noticeable. These cases will be considered later.

If one assumes that there are no intrinsic surface states present in CdTe 26 , then in consideration of the Schottky model, one can achieve, in general, good agreement between the metal work function (ϕ_m) and the Schottky barrier height (ϕ_b). For metals of high ϕ_m we generally see high barriers, an example of this is Au. Metals with work functions less than the electron affinity for CdTe ($\chi_{CdTe} = 4.28$ eV 27) show very low barrier or ohmic behaviour. Examples of this behaviour are In, Al and Ag. If we discount the result for Ni, then all the other metals so far studied on CdTe adhere to the Schottky model, with a value of S , the index of interface behaviour close to unity. The values of ϕ_m used here are all for polycrystalline metals 28 . However it is not clear, in view of the amount of intermixing that occurs at the metal/CdTe interfaces, just how relevant the values of ϕ_m are. It is possible that the metal deposition procedure may cause changes in these metal work functions.

In, Al and Sn are particularly interesting. On deposition of very small amounts of metal, the Fermi levels shift up the band gap near to the conduction band edge. This is consistent with the metal atoms acting as surface or bulk shallow donors. If we assume in-diffusion of metal atoms to a distance of the order of the escape depth giving rise to shallow donors then the results achieved for the three metals can be explained by the Fermi level at the surface being located very near to the conduction band edge, as represented by the inset in Figure 1(b). As the metal contact further grows on the surface charge transfer now occurs from these shallow donors to the surface metal resulting in the Fermi level moving back down the band gap. For In and Al the Fermi level moves close to its original position to form ohmic contact further grows on the surface, charge transfer now occurs band gap to form a low Schottky barrier, consistent with the Schottky model predictions.

The reason for Ni being inconsistent with the Schottky model is, as yet, unknown. There is a need to study further the interfaces formed between transition metals and the vacuum cleaved (110) face of CdTe, to further probe the validity of the Schottky model with respect to CdTe.

Conclusions

1. The interfaces formed between various metals and the vacuum cleaved (110) face of CdTe are non abrupt, with interface

- widths in some cases distributed over some hundreds of angstroms.
2. All metal overlayers on CdTe are polycrystalline in nature.
3. Defects do not appear to play an important role in controlling Schottky barrier formation.
4. Despite the presence of non abrupt interfaces and the associated defects the model which best fits the experimental results for metal-CdTe systems is the Schottky model, with a value of S , the index of interface behaviour, close to unity.

Acknowledgements

M H Patterson wishes to thank the European Research Office of the United States Army for support.

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METAL-CdTe INTERFACES

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We discuss the detailed formation of Schottky barriers at interfaces between a range of metals and atomically clean surfaces of CdTe, prepared by cleavage in ultra high vacuum. The microscopic aspects associated with metal induced interface disorder, surface dissociation and interdiffusion of atoms across the interface have been probed by a range of methods including ultra violet photoelectron spectroscopy (UPS), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), low energy electron diffraction (LEED), and $I-V$ and $C-I$ methods simultaneously. The mechanisms responsible for Fermi level pinning are considered in detail and the importance of metal induced interfacial defects is emphasized. The modification of the Schottky barriers to vacuum cleaved CdTe is investigated using reactive interlayers, of Al or TeO_2 , between the clean CdTe surface and the Schottky contact.

1. Introduction

A correct description of the physics associated with metal-semiconductor contacts remains the subject of much debate. Since the early work of Bardeen [1] in 1947 several elegant theories have been put forward to account for Schottky barrier formation [2-6]. As yet, though, there has been very little agreement as to the most important processes involved. These theories have considered the relevance of intrinsic surface states on the semiconductor [1], metal wave function tunnelling into the semiconductor [2,3], many body effects [4] and metal induced gap states [2,5]. These theories, though, assume perfect interfaces between the metal and the semiconductor where interdiffusion between the species does not occur, and to date have had limited success in explaining experimental results. Recently it has been shown that this assumption is not universally correct and that in many cases considerable intermixing of the metal and semiconductor occurs even for interfaces fabricated at room temperature [6-8]. Recently it has been established that defects such as cation or anion vacancies, caused by this intermixing can dominate the Schottky barrier formation [7,9,10]. It has been shown that some metals disrupt the semiconductor surface by chemically reacting with it [11]. Other workers have shown that exposure of a clean semiconductor surface to an atmosphere,

such as O_2 , prior to metal evaporation can cause a change in the transport properties of the metal-semiconductor interface, in some cases as a result of doping the surface layers of the semiconductor [12,13].

In practice the formation of contacts to semiconductors often involves annealing or etching cycles and as such the metallurgy and chemistry of the interfacial layers must be important. The way that interfacial layers affect the properties of the contact is therefore of considerable interest from a technological as well as a fundamental point of view.

In this paper we report on the fabrication of contacts to the vacuum cleaved [110] surface of n-CdTe. The effect of exposure to air prior to metal deposition, and of deposition of thin layers of reactive metal between the semiconductor and the Schottky contact is monitored. The role of defects, produced by these various procedures, and now generally accepted as being relevant to the III-V semiconductor-metal systems, is considered.

2. Experimental

Cadmium telluride crystals of type n, with carrier concentrations in the 10^{16} - 10^{17} cm^{-3} range were grown in our laboratory by a vertical Bridg-

man technique. The crystals could be cleaved to reveal mirror like (110) surfaces up to 100 mm² in area. Our philosophy of experimentation is to carry out complementary surface analyses sequentially in the same ultra high vacuum (UHV) chamber on the same sample without breaking the vacuum. To facilitate this we have at our disposal three UHV chambers each capable of achieving better than 10^{-10} Torr working pressures. Techniques at our disposal included X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), low energy electron diffraction (LEED) and ultra violet photoelectron spectroscopy (UPS). These techniques were used to monitor the chemistry, metallurgy and electronic structure involved in the Schottky barrier formation. Thick film values of Schottky barrier height could be established by I - V and C - V techniques in UHV.

We characterize the vacuum cleaved (110) surface of CdTe by the techniques above. Then controlled amounts of metal are evaporated onto the CdTe surface and the early stages of interface formation monitored by XPS, UPS and AES. The film thickness is gradually increased and on the establishment of thick metal overlayers the Schottky barrier heights are established by I - V and C - V techniques. LEED was carried out on thick metal overlayers. Where reactive metals (e.g. Al) were deposited on the cleaved surface prior to unreactive metals (e.g. Au), double filament evaporation sources were used. The thickness of the metal films deposited was measured using a quartz crystal thickness monitor.

Ohmic contacts to the CdTe were made by evaporation of In onto a (110) surface followed by annealing in vacuum ($\sim 10^{-2}$ Torr) for 10 min at 175°C.

3. Results

Fig. 1 shows the values of Schottky barrier heights measured for various metals on the vacuum cleaved (110) surface and the air cleaved (110) surface of CdTe. The air cleaved surface was exposed to air at atmospheric pressure for 48 h prior to metal deposition. An XPS spectrum of a vacuum cleaved (110) surface and an air cleaved (110)

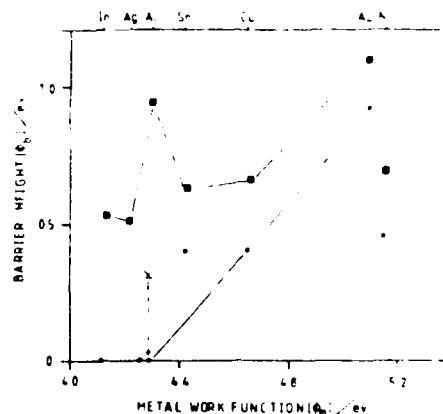


Fig. 1. Plot of barrier heights, ϕ_b , versus metal work functions ϕ_m , for various metal-vacuum cleaved CdTe (●) and metal-air cleaved CdTe interfaces (■). The electron affinity of CdTe, χ , is indicated on the plot.



Fig. 2. XPS spectra of (a) vacuum cleaved, (b) air cleaved CdTe. Inset: magnification of the Te 3d region of air cleaved CdTe. The splitting in the 5/2 and 3/2 peaks due to TeO₂ are clearly seen.

surface are shown in fig. 2. It has been shown [8] that the splitting seen in the Te 3d peaks is due to the presence on the surface of oxygen in the form of TeO_2 . From fig. 1 it is clear that this oxide layer has a drastic effect on the Schottky barriers formed on CdTe. On the air cleaved surface all metals investigated produced Schottky barriers of 0.5 eV or greater. However on the atomically clean vacuum cleaved surface all of the metals showed a reduction in the measured Schottky barrier heights, with three, In, Ag and Al producing very low barrier or ohmic behaviour. The observations on the vacuum cleaved surface can be understood to a large degree by use of the Schottky model. It has recently been indicated [14] that the deviations from the Schottky model (e.g. for Ni) occur when high work function metals are used which induce Cd outdiffusion from the semiconductor surface. This results in interface states which prevent the Fermi level at the semiconductor surface from shifting further than ~ 0.5 eV below E_c . Table 1 shows those metals which show Cd outdiffusion as the metal-semiconductor interface is formed. Clearly, although there is Cd outdiffusion associated with low work function metals, e.g. Al, the resulting levels generated within the gap do not influence the Schottky barrier behaviour. Fig. 3 shows a UPS spectra of vacuum cleaved CdTe. The spectra are measured for emission normal to

Table 1
Barrier heights, measured by I - V , of various metal-CdTe interfaces; indicated are the systems where UPS has shown Cd outdiffusion to occur on formation of the interface (vacuum cleaved surface only)

Metal	Barrier height (eV)		Cd out-diffusion	ϕ_m (eV)
	Vacuum cleaved	Air cleaved		
Au	0.96	1.1	No	5.1
Ag	Ohmic	0.5	No	4.28
Al	Ohmic	0.93	Yes	4.26
In	Ohmic	0.52	No	4.12
Sn	0.4	0.6	No	4.42
Cu	0.45	0.6	Yes	4.65
Ni	0.4	0.63	Yes	5.15

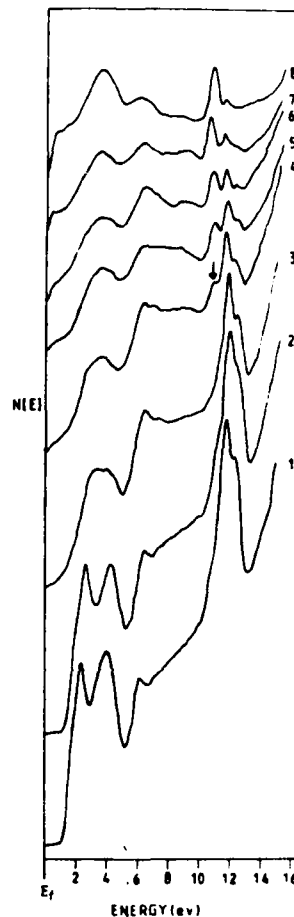


Fig. 3. Angle resolved photoelectron spectra for vacuum cleaved CdTe with controlled evaporation of Al. Spectra shown are for normal emission, $h\nu = 21.2$ eV, angle of incidence of light $\approx 55^\circ$. The peak marked with an arrow at a binding energy of ~ 10.3 eV is due to Cd outdiffusion from CdTe into the Al overlayer. Spectrum 1 shows the vacuum cleaved CdTe surface. Spectra 2-7 show the surface with gradual Al coverage. Spectrum 8 is the CdTe surface with a thick Al overlayer.

the surface ($h\nu = 21.2$ eV, unpolarized). The spectra for the clean surface shows both valence band emission as well as emission from the deeper Cd

4d orbitals. Upon deposition of Al several things of note happen: (i) At very low Al coverage, before any modification of emission of the valence band region occurs, all features in the spectra due to CdTe, shift to higher binding energies by ~ 0.2 eV. As the coverage of Al is increased the features move back to their original binding energies. (ii) At higher Al coverage one sees a new component appearing on the lower energy side of the Cd 4d emission by ~ 0.6 eV. As the Al coverage increases this feature becomes very dominant. This is chemically shifted emission from the Cd 4d orbitals which has been removed from the semiconductor surface and is incorporated in the metal overlayer. This Cd outdiffusion has been seen for other metals as well, e.g. Cu and Ni.

The Fermi level movement with increasing metal coverage, as measured by UPS, is summarised for several metals in fig. 4. Several different types of behaviour are seen. The first type of behaviour is seen with Au. Cu and Ni also show this behaviour. As the metal overlayer grows so the features of the spectra gradually move to lower binding energies indicative of a gradual movement of the Fermi level at the semiconductor surface in the gap. Silver, however, shows a behaviour where no shift of the Fermi level at the surface is seen even for fairly high metal coverages. Al and In, for low metal coverages both show a movement of all features in the spectra to higher binding energies. As the metal builds up on the surface of the semiconductor so the features move back to their original binding energies. It is known that both Al and In act as shallow donors in bulk CdTe [15]. The behaviour of these two metals is consistent with an

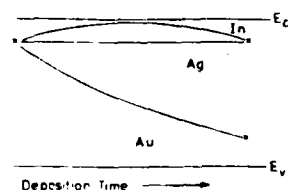


Fig. 4. Movement of the Fermi level at the CdTe surface, as measured by UPS, as various metals are progressively deposited on the clean CdTe surface.

initial indiffusion of metal atoms to produce a highly n-type layer with the Fermi level being located near to the conduction band edge. As the metal contact grows on the surface then charge transfer now occurs from these shallow donors to the metal resulting in the Fermi level now moving back down the band gap. No outdiffusion of Cd is seen with In contacts.

The electrical, I - V , characteristics of Al and Au contacts to n-type CdTe are shown in fig. 5. These two metals produce quite different barrier behaviour, consistent with the observations of UPS. The metals adhere well to the Schottky model where the barrier height is highly dependent on the metal work function.

On air cleaved CdTe however the situation is different. For all metals studied the presence of the oxide layer leads to an increase in the Schottky barrier height, as shown in fig. 1.

The I - V characteristics of an Al-air cleaved CdTe diode are also shown on fig. 5. For Al the

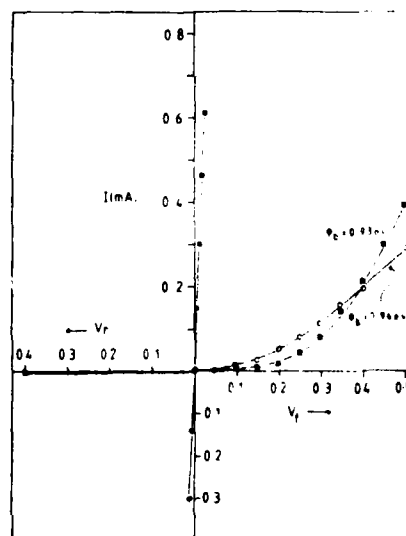


Fig. 5. Current-voltage characteristics (dC) for (●) an Al-vacuum cleaved CdTe interface, (■) an Al-air cleaved CdTe interface and (○) a Au-vacuum cleaved CdTe interface.

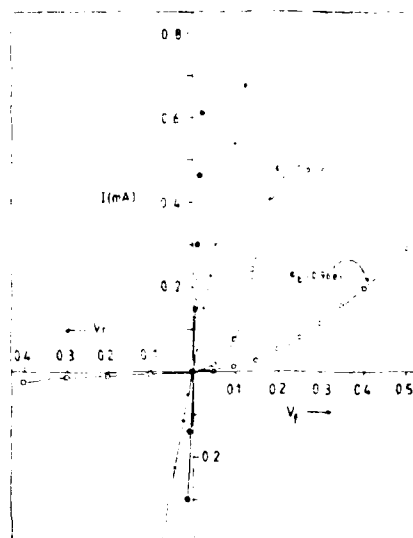


Fig. 6. Current-voltage characteristics (dC) for (●) an Al-vacuum cleaved CdTe interface, (x) a 2 Å of Al-Au-vacuum cleaved CdTe interface, (▽) a 0.8 Å of Al-Au-vacuum cleaved CdTe interface and (○) a Au-vacuum cleaved CdTe interface.

increase in barrier height is much greater than for Ag. It is obvious therefore that the use of reactive interlayers between the semiconductor surface and the metal overlayer is a way of affecting the Schottky barrier height. The possibility then arises of controlling the barrier height by appropriate control of the reactive interlayer. To this end we have used very thin interfacial layers of Al, a reactive metal, to modify the Schottky barriers formed by Au on CdTe. Fig. 6 shows the $I-V$ characteristics of diodes prepared with various Al interlayer thickness contacts. The CdTe-Al and CdTe-Au contacts are the same as in fig. 5. From fig. 6 it is seen that by having as little as 2 Å of Al between the vacuum cleaved (110) surface of CdTe and the Au contact the Schottky barrier behaviour has been drastically changed, from $\phi_b \approx 0.96$ eV to an ohmic or very low barrier contact. At lower Al interlayer thickness, 0.8 Å, one still sees an appreciable Schottky barrier, although reduced from the

value of barrier height were no Al interlayer is present.

4. Discussion

In general good agreement between Schottky barrier heights measured by $I-V$, $C-V$ and UPS techniques has been achieved for the metal-vacuum cleaved CdTe systems. We have shown that the type of Schottky barrier behaviour observed on CdTe is very dependent on both the metal and the nature of the CdTe surface. It has been noted that many of the metal-CdTe interfaces are not abrupt with interface widths being wide in some cases.

For metals on vacuum cleaved CdTe the results can be summarised and evaluated as follows. For low work function metals ($\phi_m < 4.3$ eV) the Schottky barrier height is less than 0.1 eV regardless of whether there is Cd outdiffusion into the metal contact. For metals of larger work function, with the exception of Ni and Sn, the Schottky barriers formed are in rough accordance with the linear interface potential model in the Schottky limit [16]. The Ni-CdTe system is not consistent with this behaviour. Here the Fermi level at the surface appears pinned at ~ 0.5 eV below the conduction band, an observation which suggests that a combination of cadmium outdiffusion and a high work function metal leads to the presence of states at the interface which effectively prevents the Fermi level at the semiconductor surface from shifting further than 0.5 eV below the conduction band edge. The exact nature of the states responsible for this Fermi level pinning is as yet uncertain. Several acceptor levels have been observed within the gap and the assignment of causative species to these levels have been many. Comprehensive lists of these appear in articles by Kröger [17] and by Takebe et al. [18]. The levels which are believed to be correct for Cd vacancies are at $E_c - 0.6$ to 0.7 eV for a doubly charged Cd vacancy and at $E_c + 0.05$ to 0.06 eV for a singly charged Cd vacancy. If one postulated that for the case of Ni-CdTe the Cd outdiffusion led to the presence, in a large enough concentration of, doubly charged Cd vacancies at the semiconductor interface, then the resultant pinning of the Fermi level would produce

the Schottky barrier behaviour seen.

Even though Cd outdiffusion occurs at metal-CdTe interfaces where the metal work function is low, e.g. Al, the resulting energy levels generated do not influence the Fermi levels. The importance of defects and in particular the role of the Cd deficiency in the formation of Au and Au/Cd contacts to CdTe has recently been recognised [19]. The Sn-CdTe system is one where agreement between I - V and UPS evaluations of Schottky barrier height is not so good. I - V measurements, as shown in table I, indicate a barrier of 0.4 eV to be present. UPS, however, has shown that a lower barrier of ~ 0.3 eV has been established [14]. Until a more consistent evaluation of the Schottky barrier height for the Sn-CdTe system has been established, inclusion of it in the discussion could be misleading.

Recently the formation of metal contacts to the related II-IV compounds CdS and CdSe has been studied [20]. It was noted that many of the interfaces studied were non-abrupt with, in some cases, appreciable interface widths. The use of ultra thin layers of a reactive metal, Al, between the semiconductor and the Schottky contact, Au, led to appreciable modification of the Schottky barrier behaviour. This modification was very sensitive to the thickness of the Al interlayers. It was concluded that the modification in Schottky barrier height was dependent on the density of metal induced surface states rather than on a qualitative change in the nature of these states. The question must then be asked as to whether a similar philosophy can be applied to the results observed for thin interlayers of Al between the CdTe and the Au contact. It is known that Al can act as a shallow donor at $E_c - 0.014$ eV [15] in bulk n -type CdTe, so that near surface doping could generate similar states at the interface. If the density of these states is large enough then a highly n -type surface layer of CdTe may ensue with the Fermi level being located very near to the conduction band edge. Our UPS results have shown that a movement of the Fermi level at the surface towards the conduction band is indeed seen for very small coverage of Al, prior to any evidence of metallic Al being seen on the surface. If we now deposit a thick Au overlayer onto this system then charge transfer to

the Au would occur, the result being a Schottky barrier of effective height less than that observed for the simple Au-CdTe system due to tunnelling through the very thin region of the barrier at the interface. This type of result is seen with an Al interlayer thickness of 0.8 Å. An increase of the Al interlayer thickness of 2 Å produced contacts ohmic in nature. This result would indicate that one now has a metallic Al overlayer on the surface. Although the Fermi level at the surface has moved nearer to the conduction band due to the Al atoms acting as shallow donors, one now has charge transfer occurring between the semiconductor and the metallic Al overlayer rather than the subsequently deposited Au, the result being a contact that is ohmic in nature.

One must also consider the possibility of the formation of "islands" of Al on the CdTe surface at very low Al coverages. Deposition of an Au electrode on top of this would result in an electrical contact of "mixed phases" where different types of Fermi level pinning behaviour occur. A recent theoretical treatment [21] of mixed phase contacts has shown that where a contact exists in which there are phases showing different Fermi level pinning behaviour, interactive effects are such that in measuring the contact characteristics one would only see one averaged Fermi level position.

If for 0.8 Å of Al we postulate the presence of Al islands on the CdTe surface then subsequent deposition of Au will lead to a "mixed phase" contact. The electrical characteristics of this contact can be understood as being consistent with the Fermi level averaging concept.

With 2 Å of Al between the CdTe and the Au the situation is different, and we assume that the Al patches have now developed into a smooth continuous film of atomic thicknesses. If 2 Å of Al forms such a film on the CdTe, then even with the subsequent deposition of Au on top of the Al, one would only have a single phase contact, that of the Al to CdTe Fermi level pinning behaviour. Resulting in an ohmic or very low barrier contact.

Introduction of oxide layers between the metal contact and the clean CdTe surface also modifies the Schottky barrier behaviour. Oxidation of the CdTe results in the formation of TeO_2 on the surface. For all metals studied the Schottky barrier

increases when an air cleaved surface is used instead of a vacuum cleaved one. The increases however are not all of the same magnitude. Several processes may contribute to this. Firstly disruption of the CdTe caused by the oxidation process may give rise to surface states, thus affecting the Fermi level at the semiconductor surface. Secondly, impinging metal atoms may react chemically with the surface TeO_2 to form metal oxide overlayers, a process which is energetically favourable for several of the metals involved, e.g. Al, In, Cu, Sn and Ni. This may lead to a change in the work function of the overlayer. It has been reported [22] that exposure of Indium metal to air at atmospheric pressure increases the work function from ~ 4.1 to ~ 4.6 eV. In 1960 it was reported [23] that the work function of outgassed Ni was ~ 5.1 eV, but that the work function of outgassed NiO was ~ 5.5 eV. However, more recent work [24] has suggested that exposure of clean Ni(110) to oxygen resulted in island growth of NiO with a resulting decrease in work function. Hence it is difficult to know exactly what work functions to consider when metal-air cleaved CdTe systems are being considered.

These uncertainties mean that elucidation of the dominant driving force behind Schottky barrier formation on air cleaved CdTe is still far from being understood and that much more work is necessary to enable progress to be made.

5. Conclusions

(1) Interfaces formed between various metals and the vacuum cleaved (110) surface of CdTe are non-abrupt.

(2) Provided one eliminates the case of Cd out-diffusion into high work function metals, the data adhere closely to the linear interface model in the Schottky limit. It should be noted that this conclusion is based on the results of six metal-CdTe systems. To clarify the Schottky barrier formation process further, it will be necessary to investigate more metal-CdTe systems.

(3) For the Al interlayer contacts, two possible mechanisms may be responsible for the observed effects. (a) Indiffusion of Al with a resulting bar-

rier reduction, or (b) island growth at low coverages of Al leading to "mixed phase" contacts resulting in an "averaged" Schottky barrier height. Further investigations will be necessary to clarify the situation.

(4) Oxide layers on the surface of CdTe lead to increase in the measured Schottky barrier height for all metals studied. The complexity of the systems however are such that much more data will be needed to adequately describe the dominant mechanisms responsible for these effects.

Acknowledgement

The authors would like to acknowledge the support of the European Research Office of the United States Army.

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introduces uncertainty into making quantitative estimates. However, from the simulation results, there should be a total offset of at least 0.08 nm and a total relaxation of at least 0.11 nm at each interface.

Although the relaxation just mentioned may be thought of as divided between the two sides of an interface, the size is quite large—in fact as large as at a free surface. Several factors might contribute in varying degrees to such a relaxation. First, any factor that influences a free surface might also influence the interface. More specifically, bond lengths will differ at the interfaces as noted by Saris *et al.*, and, in addition, the bonds at the interfaces will differ in electronegativity.¹⁰ Another factor is the manner in which valence and conduction bands match up on the two sides of the interface.¹¹ The structure of the energy bands for InAs and GaSb can be expected to lead to charge transfer across the interface and a resulting dipole.

This research was sponsored by the Division of Materials Sciences, U.S. Department of Energy under contract W-

7405-eng-26 with the Union Carbide Corporation.

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Fermi level pinning at metal-CdTe interfaces

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(Received 22 October 1981; accepted for publication 24 December 1981)

Schottky barrier formation has been studied for a range of metals on vacuum cleaved CdTe surfaces, using a multi technique approach. Provided one eliminates the situation of cadmium outdiffusion into high work function metals from the analysis, then the data are far closer to the Schottky limit than previously reported. The influence of defects is discussed in the light of recent data relating to Au-Cd alloy contacts.

PACS numbers: 73.30. + y, 73.40.Ns, 79.60.Gs

Detailed studies of metal films deposited onto atomically clean semiconductor surfaces are gradually and progressively leading to a substantial improvement in our understanding of those mechanisms of importance in Schottky barrier formation.¹⁻³ Recent studies on clean cleaved surfaces of some III-V materials have led to the conclusion that many anomalies in our understanding of barrier formation can be removed by assuming that simple defects, such as anion and cation vacancies at the interface, can play a dominant role.^{2,4,5} In order to understand in a more general way the role played by defects it is essential therefore to extend to other semiconductor-metal systems the type of studies so successfully carried out on the III-V materials. Extension to the II-VI solids is highly desirable, and of these CdTe is particularly appropriate, since it can be doped both *n* and *p* type and can also be readily cleaved to yield high quality (110) surfaces.⁶ In these studies we have probed Schottky barriers formed by a range of metals on clean cleaved (110) surfaces of CdTe and we show that a substantial improvement in the understanding of these interfaces is obtained once the importance of defects is recognized. Indeed in a recent study of Au and Cu-Cd alloys on CdTe (Ref. 7) the

importance of defects was also pointed out.

Both *n*- and *p*-type CdTe crystals are grown in our laboratory by a Bridgman method. *n*-type crystals were cleaved in ultrahigh vacuum ($\sim 10^{-10}$ Torr) and studied by means of *x* ray and ultraviolet photoelectron spectroscopy (UPS). Metals were then deposited in successive submonolayer amounts. The formation of the Schottky barrier and interface chemistry was monitored after each deposition. We emphasize that in these studies the use of incident electron beams (LEED and Auger electron spectroscopy) was avoided, since it has been shown previously⁸ that such beams have a detrimental effect on the order and composition of the interface. Following deposition of thick (~ 1000 Å) films the Schottky barrier heights were established, *in situ*, by conventional *C-V* and *I-V* techniques.

Figure 1 illustrates a typical result, in this case for nickel on CdTe. The figure shows UPS spectra measured for emission normal to the surface ($\theta_{\text{em}} = 21.2$ eV, unpolarized). The spectrum for the clean surface shows both valence-band emission as well as emission from the deeper lying Cd4d orbitals. Upon deposition of nickel several things happen. (a) All features corresponding to emission from CdTe shift to

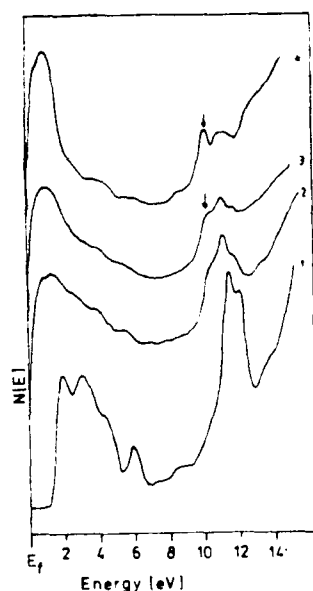


FIG. 1. Angle resolved photoelectron spectra for vacuum cleaved CdTe with controlled evaporation of Ni. Spectra shown are for normal emission, $h\nu = 21.2$ eV, angle of incidence of light = 55° . The peak marked with an arrow at a binding energy of ~ 10.3 eV is due to cadmium outdiffusion from the CdTe into the Ni overlayer. Spectrum 1 shows the vacuum cleaved CdTe surface. Spectra 2 and 3 show the CdTe surface with progressive Ni coverage. Spectrum 4 is of the CdTe surface with a thick Ni overlayer.

lower binding energies by ~ 0.4 eV as the Schottky barrier forms. (b) The emission in the valence-band region is modified as emission from the nickel becomes dominant. (c) The emission corresponding to the Cd4d levels is split with a new component appearing at a binding energy smaller by 0.6 eV. This is due to the removal of cadmium from the semiconductor and its incorporation in the metal overlayer. This effect has been seen by other workers.⁸ It is of considerable interest to note that the Schottky barrier subsequently measured by I - V and C - V methods for a thick nickel film also yielded a value of ~ 0.4 eV in excellent agreement with the photoemission observation (a), above. This was indeed found to be true for all the metals studied.

Table I summarises the measured barriers for a range of metals on CdTe and also indicates those where outdiffusion of Cd was observed. In Fig. 2 a plot of barrier heights against

TABLE I. Barrier heights, measured by I - V and UPS, of various metal-CdTe interfaces.

Metal	Barrier heights (eV)		Cadmium outdiffusion at the interface	ϕ_m (eV)
	I - V	UPS		
Au	0.92	0.85	No	5.1
Al	Ohmic	Ohmic	Yes	4.26
Ag	Ohmic	Ohmic	No	4.28
In	Ohmic	Ohmic	No	4.12
Sn	~ 0.4	0.3	No	4.42
Cu	~ 0.4	0.2	Yes	4.65
Ni	~ 0.45	0.4	Yes	5.15

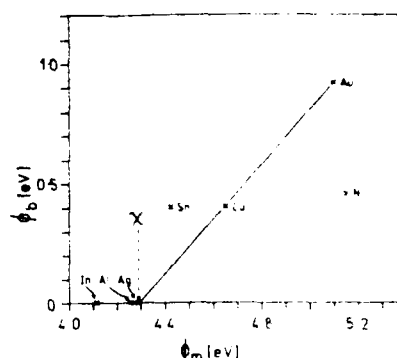


FIG. 2. Plot of barrier heights ϕ_b vs metal work function ϕ_m for various metal-CdTe interfaces. The electron affinity of CdTe, χ , is indicated on the plot.

the work function ϕ_m of the metal is shown. The values of ϕ_m have been taken from Ref. 9. This figure may be understood as follows. For low work function metals, the Schottky barrier height measured is less than 0.1 eV regardless of whether there is Cd outdiffusion into the metal contact. The data are quite consistent with the electron affinity χ , value of 4.28 eV reported for CdTe.¹⁰ For metals of larger work functions, with the clear exception of nickel, the barriers formed are roughly in accordance with the linear interface potential model in the Schottky limit.¹³ These findings are in sharp contrast to those reported by others.^{11,12}

It is clear from Fig. 2 that the nickel-CdTe system does not follow Schottky-like behavior; in this case the Fermi level at the surface appears pinned at ~ 0.45 eV below the conduction band E_c . We conclude, therefore, that for the case of cadmium outdiffusion and a high work function metal there exist states at the interface which prevent the Fermi level at the semiconductor surface from shifting further than ~ 0.5 eV below E_c .

Clearly even though there is cadmium outdiffusion associated with some of the low work function metals, such as Al, the resulting energy levels generated do not influence the Schottky barriers formed with these metals.

It is our conclusion therefore that metal-CdTe interfaces in general show a behavior close to the Schottky limit provided those high work function metals which are also associated with cadmium outdiffusion are eliminated from the analysis. It is of some interest to consider these findings in the light of a recent paper by Kuech.⁷ In this work it was found that gold contacts on cleaved CdTe yielded Schottky barriers of 0.65 eV but if an Au/Cd alloy was used a barrier of 0.92 eV was obtained. The importance of defects, and in particular the cadmium deficiency, was recognized, very much in agreement with the present work, although our value of ϕ_b for gold on CdTe differs from that reported by Kuech.

It is not possible at this stage to analyze in more detail the nature of the energy levels leading to pinning of the Fermi level following the depletion of cadmium from the semiconductor. However, a very large number of defect levels are known to exist in the¹⁴ band gap of CdTe and many have

associated with metal deficiencies. For the III-V semiconductors there is now strong evidence relating Fermi level pinning at interfaces to simple defects such as anion and cation vacancies.^{2,3} Although it is likely that the level formed following cadmium depletion, described above, has a donor nature, the existing state of theoretical approaches does not enable one to associate it with simple vacancies. The extension of the theoretical methods developed for III-V solids to the II-VI materials is therefore awaited with interest.

The authors would like to acknowledge the support of the European Research Office of the United States Army.

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SECTION 2

Surface Defects on Semiconductors

2.1 Introduction

The importance of surface electronic states in determining the distribution of electronic charge at and near a semiconductor surface has long been recognised and widely studied [1,2]. These states determine the nature and width of the space charge layer in the semiconductor. The relationship between these "surface" states and the "interface" states at boundaries between semiconductors and metals or insulators is still the subject of considerable interest and intense study and up to the present time there are a large number of questions which remain unresolved. Interface states between solids such as Si and SiO_2 , or between GaAs and its oxides, are of enormous technological importance and there are many applications of solids such as the III-V compound semiconductors which are being hindered by an inadequate lack of control over the nature and densities of interface states formed. This in turn reflects our poor understanding of the origin of interface states. During the last ten years or so modern surface and interface spectroscopies [3,4] such as LEED and Auger electron spectroscopy have become readily available so that much of the current experimental work in this area is aimed at obtaining a detailed understanding of the precise relationship between the types and exact location of atoms at the interface and the resulting electronic structure. A large number of these experiments involve highly detailed studies of crystallographic ordering, chemical interactions and shifts of the Fermi levels at the surface as metal or gaseous overlayers are deposited on atomically clean semiconductor surfaces [5-8]. These have shown that a large number of semiconductor-metal interfaces are complex both crystallographically and chemically and that imperfections at these interfaces can often dominate the electronic properties of the interface. In this section we consider and discuss some aspects relating to surface and interface defects on semiconductors and the way these in turn may influence electronic devices such as Schottky diodes.

Consider a very simple model of an n-type semiconductor with discrete acceptor like surface states as illustrated in fig. 2.1. The band bending V_B is related to the electron density N_0 and surface state density N_S by the equation

$$N_S = \frac{2\epsilon\epsilon_0 N_0 V_B}{e}$$

It is clear that for reasonable values of N_0 and ϵ then values of N_S of around 10^{12} cm^{-2} are associated with eV_B of the order of 1 eV. Since the density of atoms in the outermost layer is around 10^{15} cm^{-2} it may be seen that very small densities of surface states have a pronounced influence on band bending. These surface states may be acceptor or donor in nature and are often associated with broken bonds at the surface (dangling bonds) and with the termination of the bulk potential [1,2]. They may also be readily generated by the adsorption of contaminants on the surface. In addition it has recently become clear that surface defects or imperfections can also lead to donor and acceptor states in the band gap and that these in turn can dominate the distribution of charge near the surface. Fig. 2.2 illustrates some possible types of imperfections which will later be considered. It includes surface steps as well as vacancies and antisite defects both close to the surface and in the surface layer itself. Should these generate electronic states in the band gap, then a defect density of around 10^{-3} monolayer can clearly be of great importance.

In Part 2 we consider aspects of the role of defects on atomically clean semiconductor surfaces. In part 3 we consider briefly the influence of defects on adsorption of gases and vapours on semiconductor surfaces and in part 4 we deal with defects at metal-semiconductor interfaces and in particular with their relevance in pinning the Fermi level and in establishing schottky barrier heights. Since the most detailed studies have been carried out on III-V semiconductors most of our discussion will relate to these.

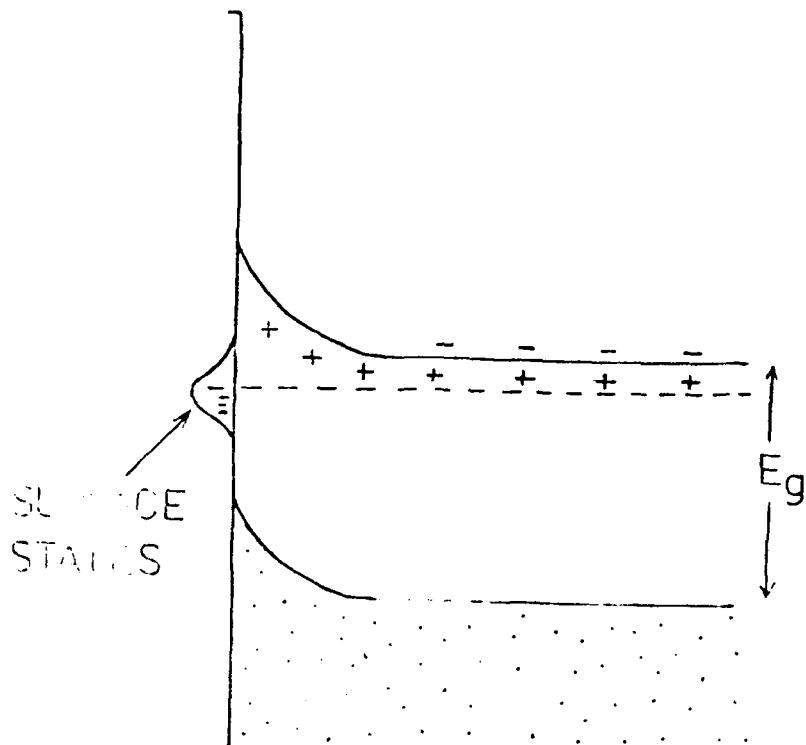


Fig. 2:1 Acceptor surface states on an n-type semiconductor leading to a depletion layer.

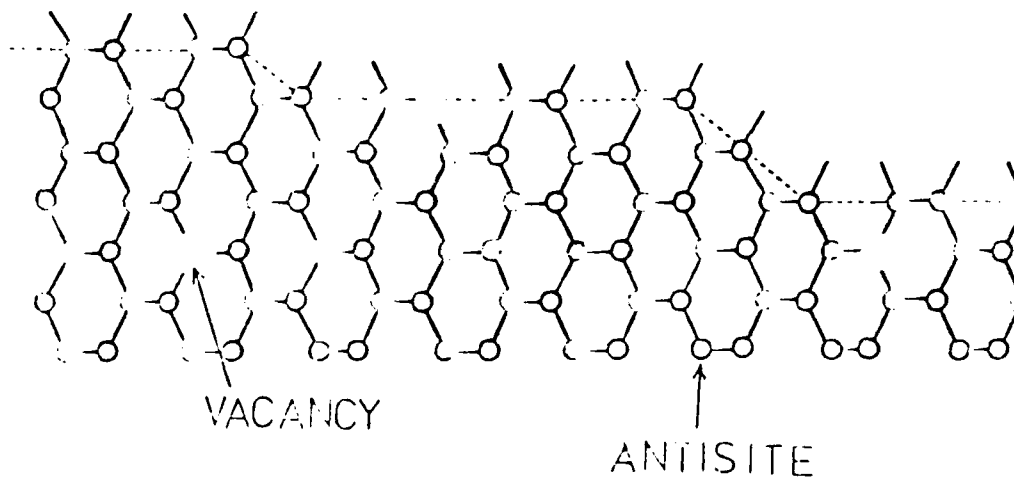


Fig. 2:2 Surface imperfections; steps, vacancies and antisite defects.

2.2 Clean Semiconductor surfaces

There have been extensive studies of surface states on clean cleaved group IV, III-V, and II-VI semiconductors. It appears that intrinsic surface states may lead to strong pinning of the Fermi level at (111) surfaces of Si and Ge [9,1]. However, for high quality cleaved surfaces of III-V compound semiconductors, such as the (110) surface of GaAs, the relaxation of the surface atoms from their bulk positions [10,11] drives the intrinsic anion and cation derived "dangling bond" bands from the gap [12,13]. Thus for a "perfect" defect free GaAs (110) surface there are no intrinsic states pinning the Fermi level at the surface and the contact potential difference between highly n-type and highly p-type crystals is roughly equal to the band gap. This means that cleaved III-V semiconductor surfaces are useful test beds to probe the effect of imperfections which generate gap states, since the defect states are not masked by intrinsic states.

It is now generally agreed that cleavage steps on GaAs (110) surfaces do generate states in the gap yielding strong Fermi level pinning on n-type crystals [14,15]. Perhaps the most convincing evidence in this regard is that produced by Monch and Clemens [15] who identified step related acceptor levels situated around 0.6 eV above the valence band edge. Little is known about the precise origin of these gap states but Joannopoulos and Mele [16] have assumed that the edges of planar (110) fractures are involved. Theoretical estimates of the energy levels associated with the resulting dangling bonds suggest the formation of occupied and unoccupied states in the gap which can account for the pinning energies. It is not possible to take this as conclusive at this stage and further microscopic studies of step profiles on such surfaces are desirable.

Step related surface and sub-surface defect states have also been observed on cleaved InP (110) surfaces by photoluminescence [17,18]. Peaks

in the spectra associated with steps have been attributed to defect levels just below the conduction band. Typical spectra are shown in Fig. 2.3.

Clearly, therefore, imperfections at and near the cleaved (110) surfaces of several III-V semiconductors lead to strong pinning effects. Many experimentalists prepare clean surfaces by heating, by ion bombardment and annealing, or by using molecular beam epitaxy to generate the substrate and associated surface. Almost invariably the Fermi levels at surfaces cleaned or prepared in this way are very strongly pinned [19-21]. There is a great deal of evidence showing that, at least for III-V materials such as GaAs and InP, sputtering and heating cycles lead to surfaces which are non-stoichiometric chemically [10] and which have a large fraction of the surface atoms, perhaps as many as 20% at step edges [22]. In addition microscopic studies [21] often show small spheres of metals (Ga or In) on the surface. The intrinsic Fermi level pinning by defects on these surfaces make them rather unsuitable for systematic studies of Schottky barrier formation with a range of metals (discussed in part 4). For example, it has been shown [19] that the Fermi level pinning is dominated by sputter induced near surface defects when Ag is deposited on a sputter cleaned GaAs (110) substrate. Likewise all metals on sputter cleaned n-type InP (110) surfaces yield very low effective barriers. Such surfaces are known to be non-stoichiometric with the surface region being deficient in the anion (phosphorus) species. It is natural therefore to consider the effect of anion vacancies on pinning behaviour. This question is pursued further in part 4.

2.3 Adsorbed layers on semiconductors

The adsorption of a gas on a semiconductor surface may alter the charge distribution near the surface and may also significantly influence the electronic nature of a contact between the semiconductor and a metal. The detailed way in which the adsorbate generates states in the gap may be complex and is very often associated in some way with surface defects. The

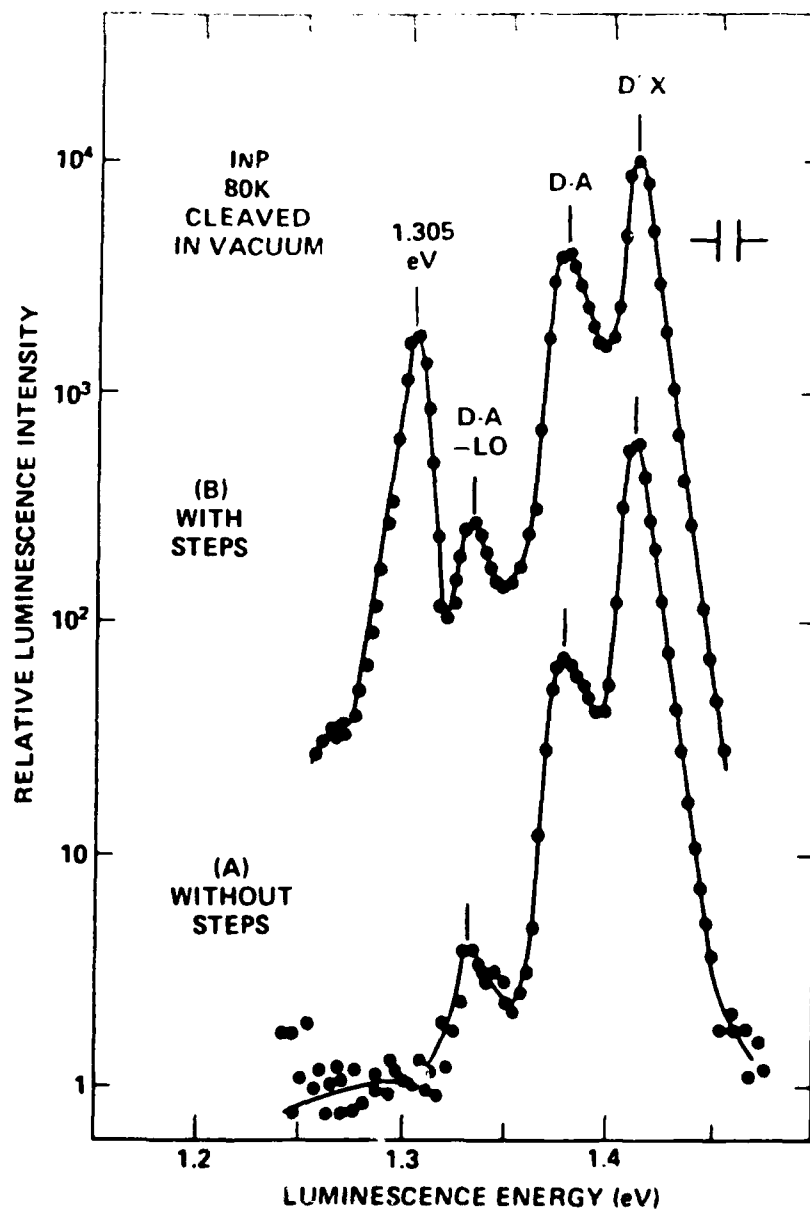


Fig. 2:3 Photoluminescence spectra from vacuum cleaved surfaces of InP. for stepped and step free regions. Note the additional peak in the upper spectrum. After ref. 17.

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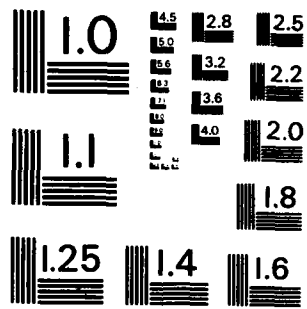
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adsorbate may generate donor or acceptor states directly following bonding to the surface, or indirectly by doping the surface region either interstitially or substitutionally, or it may create native defects such as vacancies by strong interaction with the semiconductor surface. The adsorption process itself is very often strongly influenced by surface imperfections such as steps. In particular Kasupke and Henzler [23] have clearly shown that a step density of about 15% leads to a factor of ten increase in the initial sticking coefficient of oxygen on cleaved silicon (111) surfaces. Likewise very large variations in the initial sticking coefficients of oxygen on cleaved III-V surfaces have been described in the literature, and associated with surface defects [24,25].

To illustrate the influence of step related defects on the bending of the energy bands near the semiconductor surface we again consider photoluminescence studies on cleaved InP crystals and the variation of that intensity with exposure of the clean cleaved surface to oxygen. In Fig. 2.3 photoluminescence spectra from stepped and step free regions of the InP surface were shown. Upon exposure of the step free region to oxygen the intensities of all peaks are first substantially attenuated and then recover as illustrated in fig. 2.4. The attenuation is partly associated with increased surface recombination and with increased band bending. The major part of the dip in intensity in fig. 2.4 is due to the formation of a depletion layer as shown. In this case the adsorbed oxygen (highly electronegative) forms acceptor states on the surface. The surface charge here corresponds to less than 10^{12} electrons per cm^2 . With further exposure the oxygen begins to disrupt the surface, and certainly leads to a highly disordered surface layer with a high density of defects. These defects in turn are believed to pin the Fermi level near the conduction band. For step free regions the movement of the Fermi level measured by photoelectron spectroscopy [26] follows the same trend with oxygen exposure as that shown

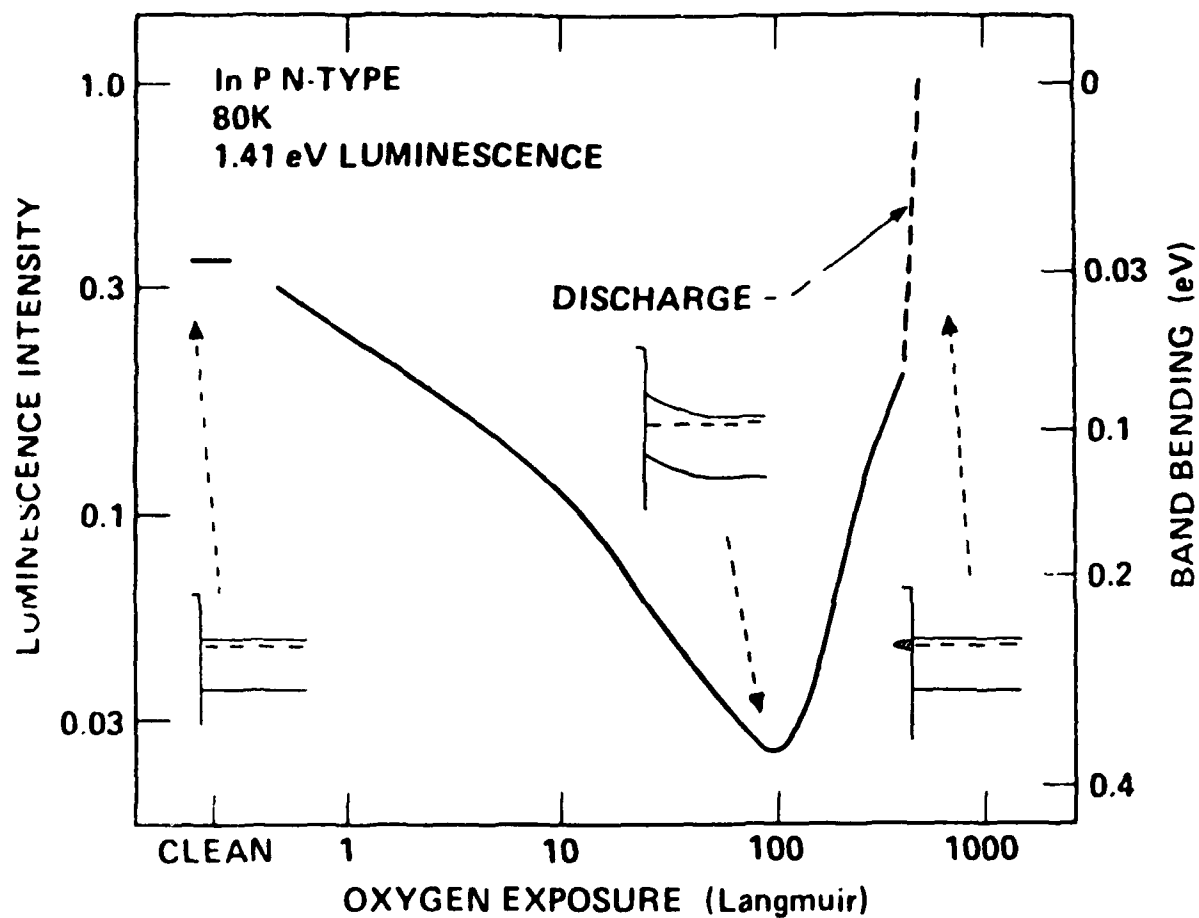


Fig. 2:4 Variation of photoluminescence intensity with exposure to oxygen, for step free regions of InP. The corresponding band bending is also shown. After ref. 17.

in fig. 2.4. For the stepped regions, however, the dip shown in fig. 2.4 is not pronounced. The interpretation is that the step induced defects pin the Fermi level in such a way that it cannot move upon exposure to oxygen.

From the above discussion, therefore, we see that surface defect such as steps and vacancies can severely influence the adsorption and interaction of gases with a semiconductor surface. The adsorption process in turn can generate surface defects, and the adsorbed species and surface defects, adsorbate induced or otherwise, can all lead to energy levels in the gap and to Fermi level pinning. In view of the complex nature of these processes it is not surprising that our understanding of them is at a very elementary stage. There is a great need for microscopic surface analytical techniques to be fully developed and applied to these problems and indeed there are indications that this will be achieved during the next few years [27].

Adsorption induced defects states on semiconductor surfaces can have a pronounced effect on the Schottky barrier when metal contacts are deposited on these surfaces. This is illustrated [28] in fig. 2.5. Here we show AES and LEED for a clean InP surface and following the exposure of the surface to water vapour. We also show the I-V curves for diodes formed by depositing Ag on the clean surface and on surfaces exposed to water. The effective lowering of the Schottky barrier has been associated with adsorbate induced defect levels. The water vapour is believed to adsorb dissociatively in part and indeed defects may also play a role in this dissociation process. There are other examples of similar effects when H_2S is adsorbed on InP [29] and on GaAs [30,31].

2.4 Metals on semiconductors

2.4.1 Perfect and imperfect interfaces

During the past few years there have been many detailed studies of the interaction of metals with semiconductors, making use in particular

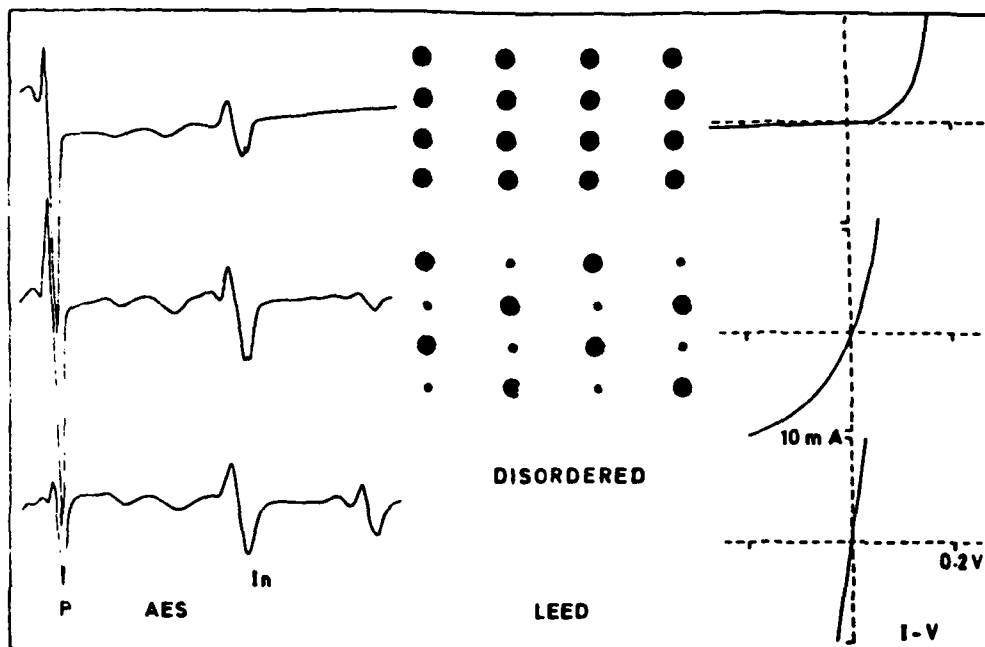


Fig. 2:5 Auger electron spectra (left) and LEED (centre) for clean cleaved InP (upper) and following progressive exposure to water vapour (10^5L , centre and 10^9L , lower). On the right are I-V characteristics when silver is deposited on the corresponding surface. After ref. 28.

of modern surface electron spectroscopies such as Auger spectroscopy (AES) and photoelectron spectroscopy (UPS) often with synchrotron radiation as the exciting source. These studies have shown beyond doubt that the intimate interface formed at room temperature between atomically clean metals and semiconductors are complex regions which very often are not atomically abrupt nor indeed fully ordered. These observations have led to theoretical viewpoints of the interface which take into account imperfections and defects and which assume that in many instances defects such as vacancies or substitutional and interstitial impurities dominate the electronic nature of the interface. Indeed Andrews and Phillips [32] in 1973 grouped interfaces into categories which included (a) weakly interacting systems (e.g. where the metal is physically absorbed on the semiconductor), (b) systems where the metal and semiconductor interdiffuse (with the metal "doping" the semiconductor), and (c) systems where the metal and semiconductor interact very strongly giving rise to new chemical products at the interface.

An interesting illustration of the difference between (a) and (c) above has recently been reported by Hughes et al. [33]. A range of metals were deposited on atomically clean cleaved surfaces of the semiconductor GaSe. This solid has a graphitic like layered structure in which the surface bonds are saturated, leading to an inert and highly perfect surface. Photoemission from the valence bands and from Ga3d and Se3d core levels were then recorded both for the clean surface and with progressive deposition of Al on the surface. Fig. 2.6a shows typical results for the case of an Al overlayer. It may be seen that emission from the Ga3d and Se3d core levels are slowly attenuated as the Al thickness increases. However, as the thickness increases beyond around 8 \AA a chemically shifted component of the Ga3d emission appears, and grows with increasing thickness. Clearly the Al is now chemically

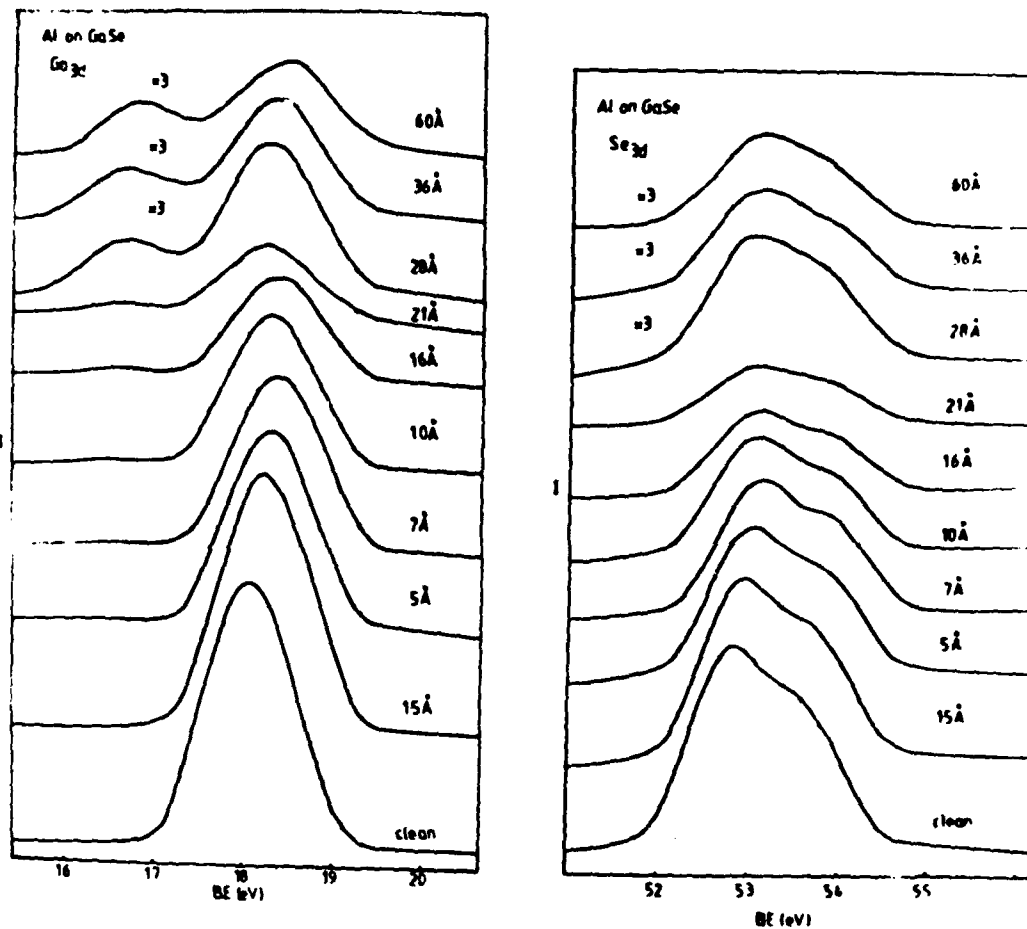


Fig. 2:6 (a) Core level soft X-ray photoemission spectra from the 3d level of Ga and the 3d core of Se for a clean surface of GaSe and with progressive thickness of Al. After ref. 33.

interacting with the GaSe surface, dissociating it and releasing Ga atoms which are then incorporated in the growing Al film. Al on GaSe therefore represents a strongly interacting system which leads to a dissociated and disordered surface. In contrast when Ag and Au are deposited there is no such dissociation of the surface; the Ga3d and Se3d core levels are equally attenuated and no chemically shifted components appear. Clearly, therefore, Ag and Au on GaSe represent category (a) in the classification outlined whereas Al on GaSe represents category (c).

There are two aspects of the above work in particular that merit further comment. First of all it was observed [33] that metals which readily react chemically with Se (i.e. which have a large negative heat of reaction with Se) are the ones which most readily dissociate the surface of GaSe. Thus bulk thermodynamic data (heats of reaction), in this instance at least, appear to yield a good guide of interface interaction. This point is somewhat controversial and will be discussed again later when we consider III-V semiconductors. The second point relates to the pinning of the Fermi level at the GaSe interface. For the clean surface the Fermi level is not pinned and the bands are flat up to the surface. Deposition of metals lead to shifts from this flat band condition and these shifts are shown in fig. 2.6b. Here the horizontal axis represents ϕ_m , the work function of the metal. It may be seen that large shifts are observed for those metals which weakly interact with the surface (Au, Ag, Sn) whereas those metals which interact strongly pin the Fermi level at a constant value. It seems certain that the defects associated with the highly disordered and dissociated interfaces pin the Fermi level at this constant value. Certainly, abrupt, ordered, weakly interacting viewpoints are not appropriate for these reactive systems on GaSe and indeed there is

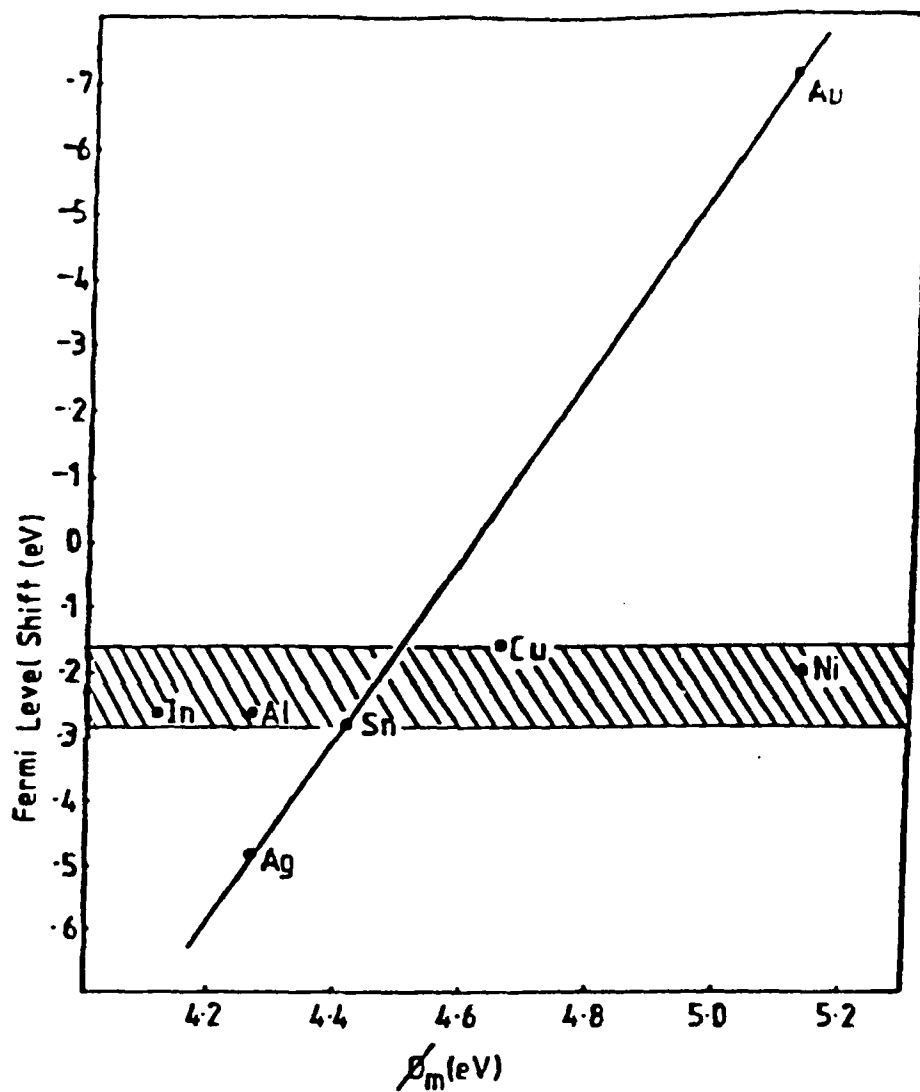


Fig. 2:6(b) Shift of the Fermi level from the flat band condition for a number of metals on clean cleaved GaSe surfaces. The horizontal scale represents the metal work function. After ref. 33.

strong evidence that this is so for many metals on group IV, III-V and II-VI semiconductors.

The above data for weakly interacting metals on GaSe are in rough accordance with the linear model of Schottky barrier formation in the Schottky limit. The linear model relates the barrier height to ϕ_m by:

$$\phi_b = S(\phi_m - \chi_{sc}) + C$$

where C is a constant, χ_{sc} the electron affinity of the semiconductor, and S a constant for a given semiconductor. Thus in the Schottky limit [34] $S = 1$, whereas in the Bardeen limit [35] $S = 0$. It may be seen however that a value of $S \sim 0$ rather than $S = 1$ is more appropriate for the reactive metals on GaSe and clearly a constant value of S for all metals, reactive and unreactive alike, is quite inappropriate. It has been shown that considerable care must be exercised in the application of the linear model to metal-semiconductor systems. It has been widely applied in the literature but often its use has been on a very uncertain and doubtful basis. The linear model formed the basis of the classification of metal-semiconductor systems in the work of Kurtin et al. [36]. In that classification S was plotted for a whole range of semiconductors [37] as a function of the ionicity of that semiconductor (defined as the electronegativity difference between anion and cation in the semiconductor, e.g. between Ga and As in GaAs). It was suggested that S values close to zero were appropriate for covalent solids such as Si, InP and GaAs but that values of S around unity applied to ionic solids such as ZnS or SiO₂. A well defined transition was suggested at a critical electronegativity difference. The basis of this classification now, however, appears uncertain. Schluter [38] has reanalysed much of the original data and shown that such a transition is not well defined. In addition it has been shown that solids such as InP [39], CdTe [40] and GaSe [33] do not yield values of S in accordance with the classification

of Kurtin et al. [36] and that in these cases the linear model is not universally applicable.

To summarise, therefore, it seems clear that many metal-semiconductor interfaces are not atomically abrupt or fully ordered, and in order to account for the electrical nature of such interfaces models which take into consideration imperfections are most appropriate.

2.4.2. Chemical Reactions and Interdiffusion

In the previous part the apparent relationship between Fermi level pinning and the nature of the metal-semiconductor interaction was illustrated. A similar behaviour is also often seen for metals on III-V semiconductors. In fig. 2.7 the Fermi level pinning positions for a range of metals on n-type GaAs [41] and on n-type InP [42] are illustrated. On GaAs all metals shown as well as oxygen seem to lead to a constant pinning energy just below mid-gap. Even metals such as Au and Cs, which have a large electronegativity difference, lead to similar pinning energies. This behaviour led Spicer et al. [41] to propose the "defect model" of Schottky barrier formation, i.e. they assumed that Fermi level pinning is caused by states in the semiconductor generated by interactions with the various metals. Since some of these interfaces were shown to be non-abrupt it was concluded that pinning was by defect states in the semiconductor near the interface. Williams et al. [39] arrived at a similar conclusion in their studies of Schottky barrier formation on InP. It seems that in this case highly reactive metals such as Ni lead to pinning of the Fermi level fairly close to the conduction band whereas unreactive metals such as Au and Ag lead to pinning energies closer to the centre of the band gap.

The difference in the nature of the chemical interaction experienced by InP when Au and Ni overlayers are deposited is illustrated in fig. 2.8. Photoemission from the In4d and P2p core levels are shown both for the

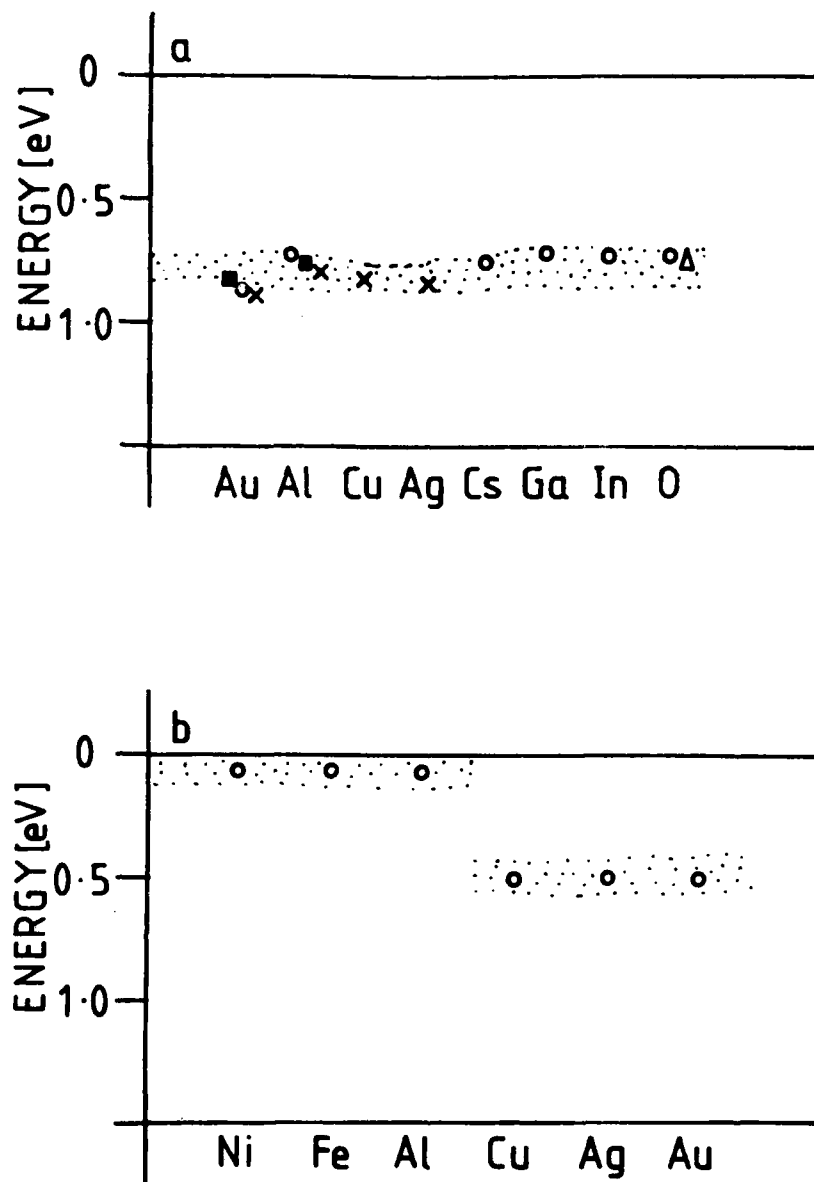


Fig. 2:7 (a) Fermi level pinning positions for a range of metals on n type GaAs. After ref. 39 and references therein.

(b) Fermi level pinning for a range of metals on n type InP. After ref. 39.

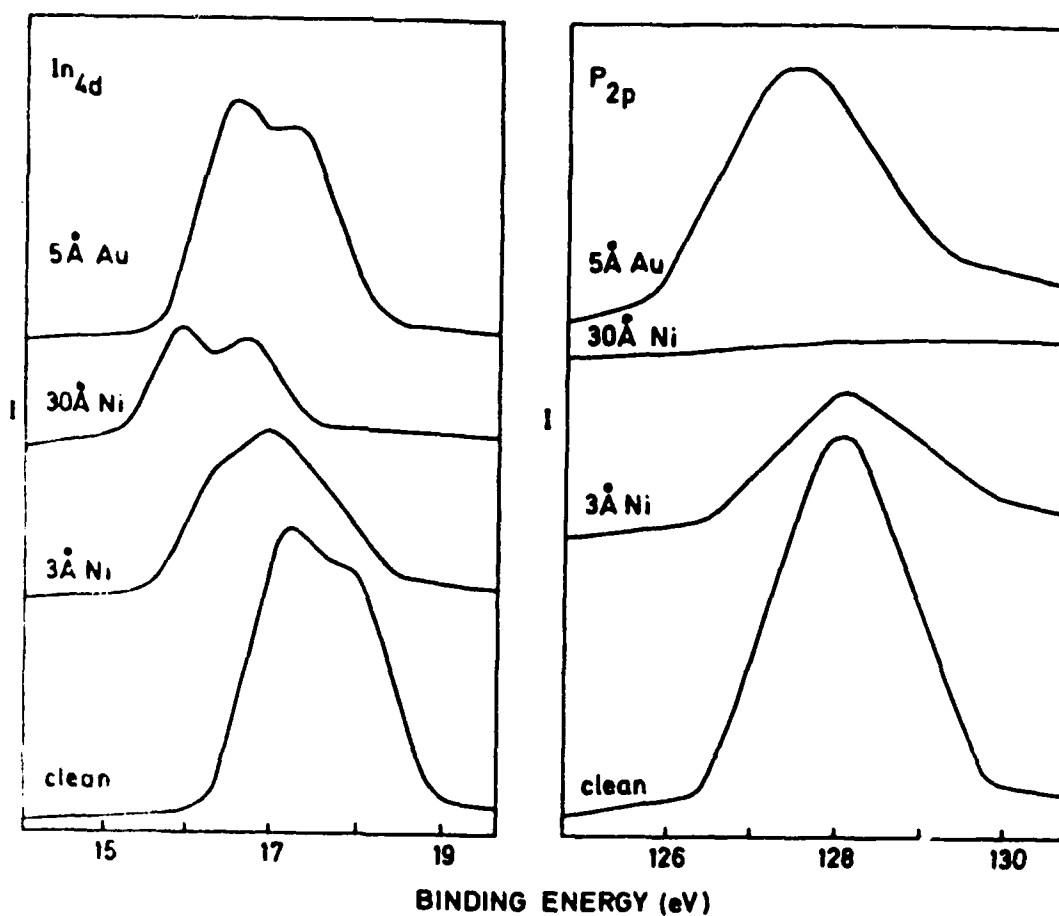


Fig. 2:8 Soft X-ray core level photoemission spectra for clean cleaved InP and following deposition of Au and Ni. After ref. 43.

clean surface and following the deposition of Ni and Au. With progressive Au deposition the In4d and P2p core levels are attenuated more or less equally and no chemically shifted components are seen (other than Fermi level shifts). The behaviour of Ni is totally different. Here the phosphorus emission is attenuated very rapidly, whereas a chemically shifted component of the In4d emission persists following the deposition of relatively thick Ni films [43]. Clearly the Ni metal interacts with the InP in such a way as to dissociate the InP surface and release In atoms which are then incorporated in the Ni overlayer.

There are two major questions which we wish to address relating to metal-semiconductor interactions of the kind illustrated in fig. 2.8. These related to the "interface width" and also to whether or not bulk thermodynamic values such as heats of reaction are of use in determining the interactions at the interface. We will take the second question first.

Brillson [44] and Brillson et al. [45] have attempted to relate Schottky barrier formation for metals on III-V semiconductors to the heat of reaction of the metal atom forming the overlayer with the anion species. Thus Al has a larger negative heat of reaction with As than does Ga so that for Al on GaAs it is likely that Ga will be replaced by Al in the surface layer. However, the usefulness of this approach has been strongly challenged by Bauer et al. [46], who studied the surface dissociation involved when Au, Ga or Ge were deposited on AlAs (110) and (100) surfaces. By comparing the data obtained with similar studies on GaAs (110) surfaces, Bauer et al. [46] concluded that bulk thermodynamic data was not a useful guide and that "local interactions" determine whether or not the interface will dissociate upon deposition of a metal overlayer. However, it should be noticed that Bauer et al. [46] compared measurements for metals on cleaved GaAs surfaces with those on

AlAs films grown by molecular beam epitaxy. It is known that slight deviations of the semiconductor surface from stoichiometry [47] as well as defects such as steps [5] or vacancies can strongly influence such interactions and it is not clear that the precise nature of the AlAs surface prepared by Bauer et al. [45] was comparable to those of cleaved GaAs in this respect. In their detailed studies of metal-cleaved InP interactions Williams et al. [43] showed that bulk heats of reaction did give a useful guide to interface chemistry. However, if the semiconductor surface was slightly sputtered by argon ions, the detailed interactions with metals subsequently deposited were drastically influenced [5] though the surface stoichiometry and order was hardly changed by the very light sputtering event. From these studies we conclude that for metal overlayers on a high quality cleaved surface of a given semiconductor, bulk thermodynamic quantities do yield a useful guide of whether or not chemical interactions will take place, at least in a limited number of cases, but such interactions may be readily influenced by deviations of the surface from perfection. There is at the present time considerable interest in the initiation of chemical interactions at interfaces such as Al-GaAs [47] and Al-InP [48]. There is strong evidence that in many instances exchange reactions do not occur until the metal coverage exceeds $1 \text{ } \overset{\circ}{\text{A}}$ or so, and this in turn depends also on the semiconductor surface chemical stoichiometry [47]. (It may be seen that the finite metal thickness of around $8 \text{ } \overset{\circ}{\text{A}}$ is needed before strong chemical interactions are observed for the Al-GaSe system in fig. 2.6a). It has been suggested that the driving energy associated with the surface dissociation is derived from the energy released in the formation of metallic nuclei on the semiconductor surface [47-49]. Whereas this is both feasible and likely, it is certain that further detailed studies are necessary before definitive statements can be made.

We now turn to the question of "interface width". In fig. 2.8 typical attenuation of core level photoemission due to the metal adlayers was illustrated. For the case of Au and Ag on InP, for example, the attenuation of In4d and P2p emission is roughly equal, whereas following Ni deposition the P2p emission is attenuated more rapidly than the In4d. Brillson et al. [50] have assumed that an "interface width" may be defined which is given by the metal overlayer thickness necessary to attenuate the anion emission by $\frac{1}{e}$. Thus for Ni on InP, the P2p emission is very rapidly attenuated and the "interface width" is therefore small. For Ag or Au on InP the P2p emission is only slowly attenuated and the interface width is therefore large. Brillson et al. [50] then probed this interface width for a large number of interfaces and arrived at the plot shown in fig. 2.9. The horizontal scale here is the heat of reaction of the atoms forming the metal overlayer with the anion species, so that large negative heats of reaction lead to very abrupt interfaces and unreactive systems to large interface widths. If correct, this analysis is extremely important for it yields a new systematic characterisation of interfaces. We therefore examine the basis of the analysis a little further.

We note that for the case of reactive metals such as Ni on InP the In4d emission is attenuated only slowly due to the release of In from the interface and its incorporation in or on the metal contact. However the rapid attenuation of the P2p emission gives no information at all relating to interface width since the Ni atoms may penetrate into the semiconductor and this is not measured. For the case of unreactive metals it has already been noted that the In4d and P2p emissions are attenuated much more slowly than would be expected if the metal overlayer grew in a layer upon layer or laminar fashion. Because the attenuation is slow Brillson et al. [50] assume that P and In atoms are released from

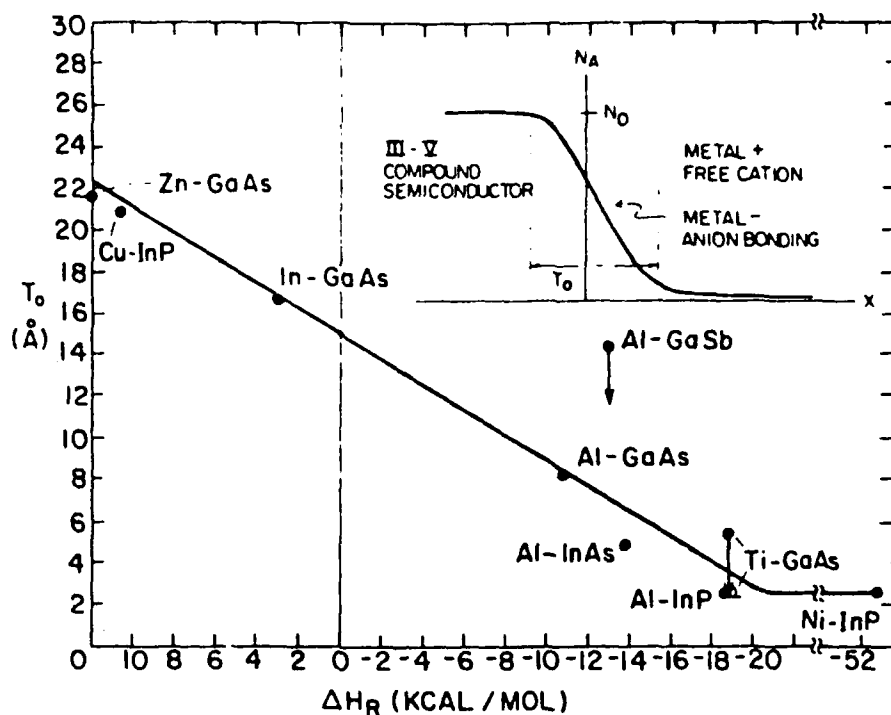


Fig. 2:9 Plot of 'interface width', T_o , against heat of reaction of the metal contact and the anion species in the semiconductor, ΔH_R , for a number of metal III-V systems as suggested in ref. 50.

the semiconductor interface and incorporated in the metal overlayer in roughly equal amounts. Thus following the deposition of say 20 \AA of Ag one still sees large In4d and P2p photoemission. It is important to note that this analysis depends entirely on the necessity for the metal to grow according to layer upon layer mode. Yet it has recently been unambiguously shown that this is not the case for metals such as Ag deposited at room temperature onto cleaved InP [5] and GaAs [51] surfaces and on GaAs surfaces prepared by MBE [52]. The growth mode involves substantial island formation (Stranski-Krastanov mode). In this situation the attenuation of the substrate core level emission must be less rapid than for the case of a layer upon layer growth mode, because substrate emission will persist from the regions in between the islands. We conclude therefore that the basis on which interface widths are established by Brillson et al. [50] are of doubtful validity and plots of the kind shown in fig. 2.9 are not useful. Indeed detailed studies of Ag-GaAs [51,52] and Ag-InP [5] interfaces by several workers recently have failed to show that these interfaces are non-abrupt, provided the metal is deposited at room temperature onto high quality surfaces. Indeed for metal-InP (110) systems it has been suggested that Ag and Cu-InP interfaces may be more abrupt than Ni-InP ones in complete contradiction to fig. 2.8 [53]. We conclude therefore that analyses of interface widths along the lines adopted by Brillson et al. [50] are not appropriate. Existing information in the literature regarding the abruptness of interfaces such as Ag-InP and Ag-GaAs (and indeed Ag-Si) is controversial and clearly requires more detailed studies for the many remaining questions to be resolved. Finally we also note that much of the photoemission evidence in the literature relating to the above questions have relied on an analysis of the spin orbit splitting of the 5d and 4d valence levels in Au and Ag respectively and differences in these splittings when the film is very thin compared to when it is

thick [46,50,54]. Smaller spin-orbit splittings at very low coverages (a few \AA) were assumed to indicate the absence of island growth. In the light of experiments where the spin-orbit splitting of the Ag4d photoemission was shown to be highly dependent on cluster size [55], it is clear that the interpretation of such variations for Au and Ag on III-V semiconductors is not conclusive and needs to be re-examined.

2.4.3 Interface defects and Fermi level pinning

As stated previously, a large number of intimate metal-semiconductor interfaces are non-abrupt and disordered and it is clear that models involving imperfections at the interface are more appropriate than those relating to ordered, perfect boundaries. In view of the fact that the semiconductor surface often becomes deficient in either the anion or the cation it is appropriate to first consider the effect of such deficiencies. For the case of InP this was first done by Srivastava [56,39] who calculated the likely energy levels generated near the surface as a result of the generation of phosphorus point vacancies. It was shown that such a vacancy could lead to an energy level close to the conduction band and that it could either donate or accept electrons. Thus, if such defects existed near the surface in sufficient number, they could certainly pin the Fermi level close to the conduction band, as observed when surfaces are sputter cleaned (with loss of phosphorus), or when they are exposed to gases such as oxygen or chlorine. The calculations carried out by Srivastava [56] employed the semi-empirical pseudo-potential method and obviously cannot be taken as highly accurate. These studies have been taken further by Daw and Smith [57-60] and by Allen and Dow [61], who have used the tight binding method. Daw and Smith [57] calculated pinning levels associated with anion and cation vacancies both when those vacancies are in the bulk and at the surface.

Again it was shown that they could have donor or acceptor nature. Of particular significance are the calculations of Daw and Smith [60] for the pinning energies in a range of III-V alloys and their results for GaAs-AlAs-InAs alloys are illustrated in fig. 2.10. The theoretical pinning energies of the bulk and surface anion vacancies are compared with the measured values and the experimental trend is clearly reproduced by the calculations. Similar trends have been observed for a number of other III-V alloy systems.

Although the calculations of Daw and Smith [57] mostly refer to anion vacancies it is normally cations that are incorporated in the contact material when metals such as Al are deposited on GaAs [62,47] or InP [63]. It appears that calculations of defect energies based on cation vacancies do not adequately account for the donor and acceptor nature of the pinning levels [57] but antisite defects, i.e. cations on anion sites should also be considered. Allen and Dow [61] have in fact used the tight binding method to calculate antisite defect energies in a range of III-V alloys and again reproduce the trends seen in experimental Schottky barrier determination. This is illustrated for the alloy $Ga_{1-x}Al_xAs$ in fig. 2.11.

There are several aspects of the "defect model" of Schottky barrier formation which deserve further comment and examination. The first relates to the accuracy of the calculations leading to trends such as those shown in figs. 2.10 and 2.11 and the usefulness of the tight binding method for this purpose. In order to calculate the defect energies it is necessary to consider several conduction bands in the calculation, and it is not clear whether or not the existing tight binding methods deal with the conduction bands in an accurate enough way or whether they include a sufficient number of them. According to Singh Lindefeldt and Zunger [64], the tight binding method is not sufficiently accurate to calculate defect energies with the accuracy

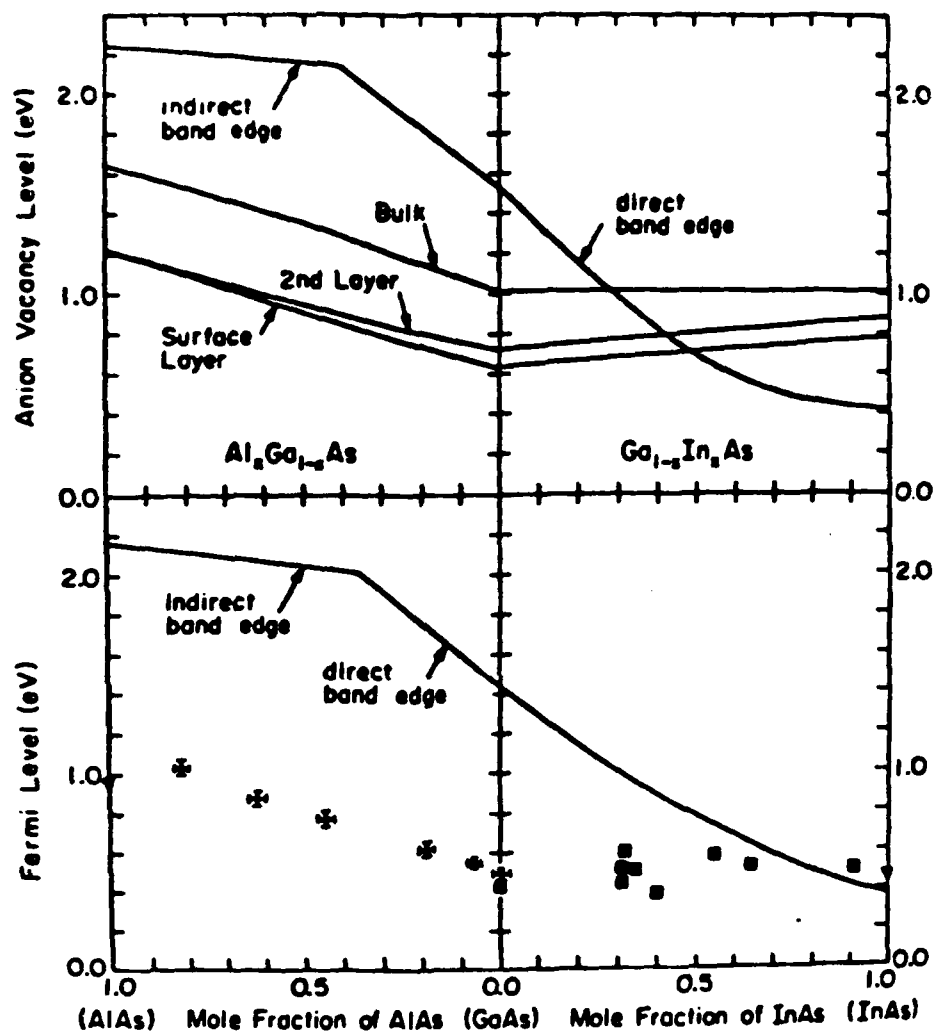


Fig. 2:10 Fermi level pinning energies, measured (lower) and calculated (upper), based on anion vacancies for the alloy systems shown. After ref. 60.

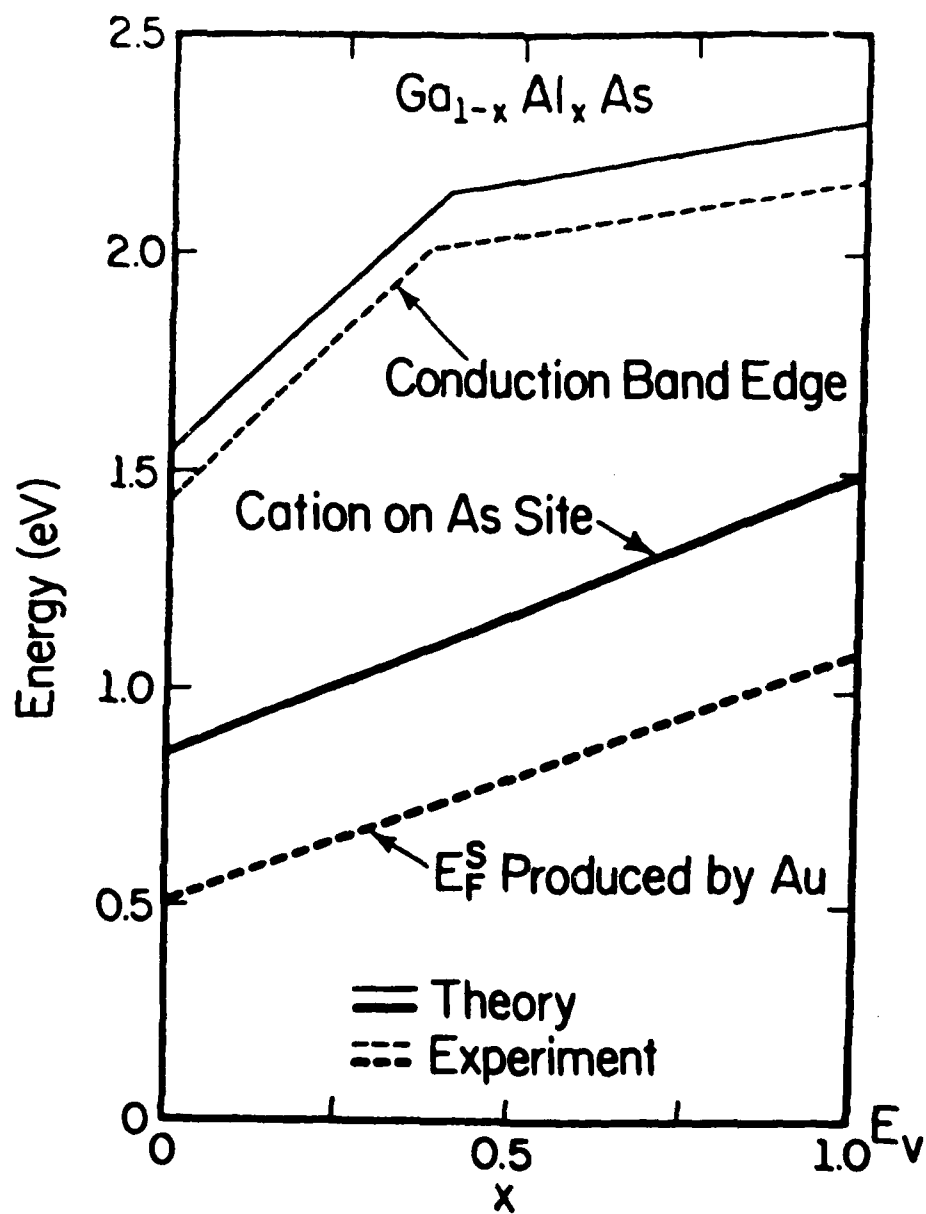


Fig. 2:11 Experimental and theoretical Fermi level pinning energies for $\text{Ga}_{1-x}\text{Al}_x\text{As}$. The calculations refer to pinning by antisite defects. After ref. 61.

necessary to confirm the "defect model". Detailed discussions of more accurate methods of calculating defect energies have been given in the literature and at the present time these methods are being refined [65,64]. Until these methods are fully applied, therefore, the question of the accuracy of the tight binding model and the usefulness of data such as those shown in figs. 2.10 and 2.11 must remain uncertain.

The second aspect of the defect model we wish to consider is the location of possible defect sites with respect to the surface. It is clear from fig. 2.10 that agreement between the pinning energies predicted by the tight binding calculations with experiment values is superior for the situation where the anion vacancy is in the surface layer, rather than in the bulk. The calculations, however, are for a free surface and do not take into account the fact that in a real situation there is a metal contact on the surface. Due to the penetration of the tails of wave functions associated with electron states in the metal, and the likelihood that a metal atom would sit in the vacancy, it is difficult to see that vacancies in the outermost surface layer are appropriate or that their energies would relate in any simple way to those calculated by Daw and Smith [57], or by Allen and Dow [61]. It is thus far more likely that the relevant defects are those in layers below the surface, and that the variation of defect energy with distance from the surface, as well as the disorder that is known to exist at many interfaces would lead to some broadened distribution of interface states. It is of considerable interest to note that the non-ideality of Schottky diodes (the " T_0 anomaly") has been associated with an exponential or parabolic distribution of interface states [66] and defects of the kind outlined above could clearly serve as the origin of such states.

Finally, we consider whether, if defect states are available at the metal-semiconductor interface in densities sufficient to cause

substantial pinning, they can be detected directly by currently popular surface electron spectroscopies such as UPS. In order to achieve pinning of the kind observed for metals on GaAs (i.e. where S is close to zero) a simple theoretical analysis [67,68] indicates that a density of interface gap states approaching 10^{14} cm^{-2} is required. If these states were confined to a fairly narrow energy range, as assumed in the defect model, then it would be anticipated that they could be detected directly by techniques such as UPS and low energy electron loss spectroscopy (LEELS). The former technique in particular is capable of probing just a few atomic layers near the surface, provided the excitation energy is appropriately chosen, and should have a high sensitivity to occupied localised states in the band gap. Remarkably, though, photoemission from surface defect levels has rarely been observed. Such localised emission has been observed by Montgomery et al. [29] for the case where clean cleaved InP surfaces were exposed to water vapour for extended periods. The exposures concerned were certainly sufficient to drastically influence Schottky barriers formed with Au and Ag contacts. Oxygen induced states in the band gap have also been observed by Thuault et al. [69] during their studies of oxygen adsorption on GaAs (110) surfaces using photoemission yield spectroscopy. Indeed in these studies it was reported that the density of oxygen induced surface states was greater than the density of oxygen atoms on the surface by around an order of magnitude and approached 10^{14} cm^{-2} at very low oxygen coverages. Bolmont et al. [51] have also observed states of this kind in the band gap of GaAs following very small coverages of Ag. However, they preferred to interpret these states in terms of an adsorbate induced change of the surface relaxation rather than in terms of adsorbate induced defect levels. Clearly, therefore, there is a need for more detailed studies of surface defects and in particular there is a need to develop and apply

techniques which can identify and characterise the defect levels and their influence on metal-semiconductor interfaces.

2.5 Conclusions

It is now well known that the existence of surface defects close to or at a semiconductor surface can have a significant influence on the distribution of electronic charge near that surface and on the way that surface interacts with gases and metals. In many instances the existence of a very small density of surface defects can trap electrons and holes on the surface and determine the magnitude of the space charge layer near the surfaces. The interactions between surface defects and the adsorption of gas on a semiconductor is often complex. The adsorption of the gas, its possible molecular dissociation, and the way it chemically reacts with the semiconductor is often controlled by the presence of surface defects. The gas-solid interaction in turn may generate more defects which can influence the electronic properties of the near surface region.

The interaction of metals with clean semiconductor surfaces often lead to interfacial layers which are disordered and which may contain new reaction products, and in addition the metal and semiconductor may intermix even at room temperature. All these processes may be influenced by the perfection of the semiconductor surface. Theories of Schottky barrier formation which assume abrupt and ordered boundaries do not describe these situations adequately; theories which take into account imperfections are more suitable and have been more successful in describing the range of experimental data obtained on III-V semiconductors. The "defect model" has been particularly successful but there are still a number of issues relating to this model which are still unresolved. There are also a number of unresolved issues relating to the experimental data and in particular to the width of imperfect interfaces.

At the present time our understanding of surface and interface defects on semiconductors at a microscopic level is at a very elementary stage. Since their existence and detailed interactions control so many surface processes there is a great need to apply and develop methods which can probe the nature of surface defects on a atomic scale.

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